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(54) Title: INHIBITION OF PULP AND PAPER YELLOWING USING NITROXIDES AND OTHER COADDITIVES			
(57) Abstract <p>Pulps or papers, especially chemimechanical or thermomechanical pulps or papers, which still contain lignin, have enhanced resistance to yellowing when they contain an effective stabilizing amount of a hindered amine compound which preferably is a nitroxide, a hydroxylamine or an ammonium salt thereof. This performance is often further enhanced by the presence of one or more <u>coadditives</u> selected from the group consisting of the <u>UV absorbers</u>, the <u>polymeric inhibitors</u>, the nitrones, the fluorescent whitening agents, metal chelating agents, sulfur containing stabilizers, metal salts and diene compounds. Combinations of nitroxides, hydroxylamines or their salts, benzotriazole or benzophenone UV absorbers and a metal chelating agent are particularly effective. Selected derivatives of 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol and selected hydroxylamine salts are novel compounds and are surprisingly effective for this purpose.</p>			

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INHIBITION OF PULP AND PAPER YELLOWING  
USING NITROXIDES AND OTHER COADDITIVES

The instant invention pertains to a method for preventing the loss of brightness and for enhancing resistance to yellowing in pulp or paper which still contains lignin by the addition of nitroxides, hydroxylamines or their salts and other coadditives. The instant invention also pertains to novel compounds which are selected derivatives of 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol or which are their hydroxylamine salts.

Background of the Invention

High-yield and ultra-high yield wood pulps undergo rapid light-induced discoloration, particularly when they are exposed to near ultraviolet light (wave lengths 300-400 nm) in indoor fluorescent light and daylight. This characteristic restricts their use to short-life, low-value paper products. High-yield and ultra-high yield wood pulps can be bleached to a high level of whiteness. If this whiteness could be stabilized against discoloration, these bleached high-yield pulps could displace significant amounts of more expensive fully-bleached, low-yield chemical pulps.

This discoloration is ascribed to the substantial lignin content of high-yield pulps totaling about 20-45% by mass. Phenoxy radicals are the key intermediates in the reaction mechanism. Several light-induced reactions have been proposed to account for their formation such as abstraction of a hydrogen atom from phenolic groups, cleavage of the aryl ether bond of phenacyl aryl ether groups, or breakdown of ketyl radicals formed from saturated aryl-glycerol  $\beta$ -aryl ether structures in lignin. The phenoxy radicals are oxidized by other oxygen-centered radicals (alkoxy, peroxy, hydroxy and perhydroxy) to form yellow chromophores. (C. Heitner in "Photochemistry of Lignocellulosic Materials", C. Heitner, J.C. Scaiano, eds., ACS Sym. Ser. 531, 1-25 (1993).)

I. E. Arakin et al., Khimiya drevesiny (Chemistry of Wood), 1982, No. 2, 114 and A. D. Sergeev et al., *ibid*, 1984, No. 5, 20 disclosed that the use of iminoxyl radicals such as TEMPO (1-oxyl-2,2,6,6-tetramethylpiperidine) is useful in the delignification of wood using the one-stage oxygen-soda (alkaline) process, but made no mention or suggestion of any activity provided by

TEMPO on preventing light-induced discoloration of paper or pulp made from such treated wood.

EP 717,143 and WO 97/36041 describe a multicomponent system for changing, reducing or bleaching lignin and lignin-containing materials which comprise a oxidation catalyst, and a N-hydroxyl mediator compound such as a N-hydroxyphthalimide or a dialkylhydroxylamine. These references are aimed at the delignification of wood. There is no mention or suggestion of any activity provided by the N-hydroxyl compounds in preventing the light-induced discoloration of paper or pulp made from such treated wood.

V. I. Khodyrev et al., Vysokomol soyed, A29, No. 3, 616 (1987) [Polymer Sci. U.S.S.R., 29, No. 3, 688 (1987)] show that the photoinitiated oxidation by oxygen causes weathering of cellulosic textile materials such as flax or cotton. The UV absorbers offer no protection, and are actually detrimental. The authors noted that the stable nitroxyl radical 1-oxy-2,2,6,6-tetramethyl-4-hydroxypiperidine interacts with alkyl radicals in the cellulose to afford its salubrious stabilizing activity. There is no suggestion by the authors that this stabilizing activity could be applied successfully in lignin-containing pulp and/or paper made therefrom.

M-K. Syker et al., J. Assn. Paper Pulp Tech, 29, 135 (1990) show that selected metal salts such as magnesium sulfate and lower alkanolic acids inhibit color reversion in bleached pulp.

P. Fornier de Violet et al., Cellulose Chem. Tech., 24, 225 (1990) show that the use of UV absorbers and hydrogen donor agents such as thiols, ascorbic acid, etc. help prevent the photoinduced discoloration of hydrogen peroxide bleached wood pulp, but that chain breakers such as hindered phenols and hindered amines (having >N-H or >N-CH<sub>2</sub>- moieties) had no or even a detrimental effect on preventing photoinduced discoloration.

R. Agnemo et al., Holzforschung (1991), 45 (Suppl), 101, confirmed that free hydroxyl radicals plus lignin lead to undesirable photoyellowing in pulp and paper.

S. Omori et al., J. Assn. Paper Pulp Tech, 48, 1388 (1993) describes the effect of antioxidants and UV absorbers on light reversion and concludes that the combination of an

antioxidant and UV absorber prevents color reversion and has a synergistic effect in that activity.

M. Paulsson et al., Nordic Pulp Pap. Res. J., (1995), 10 (1), 62-67, show that efficient photostabilization of unbleached paper or hydrogen peroxide bleached TMP pulp can be achieved by acetylation.

There have been a number of different approaches proposed to inhibiting the yellowing of mechanical pulps. These include: radical scavengers and antioxidants; UV screens; elimination of chromophores after their formation; chemical modification of lignin by alkylation or acetylation; polymeric inhibitors; and two types of coadditives used in combination. Z-H. Wu et al., Holzforschung, 48, (1994), 400 discuss the use of radical scavengers like phenyl-N-tert-butyl nitron to reduce the formation of chromophores during mechanical pulping and give a more light-stable pulp.

C. Heitner, "Chemistry of Brightness Reversion and It Control, Chapter 5", in Pulp Bleaching-Principles and Practice, C. W. Dence, D. W. Reeve, eds., TAPPI Press, Atlanta, 1996, pp 183-211, summarizes the state of the art in the thermal and light-induced yellowing of lignin-containing pulps such as thermomechanical (TMP) and chemithermomechanical (CTMP) pulps, showing the seriousness of these undesirable effects discusses generally the then current prior art methods used to attack this problem. These include bleaching, the use of phosphites, UV absorbers, polyalkylene glycols and free radical scavengers such as ascorbic acid, thiols, thioethers, dienes and aliphatic aldehydes and chelating agents such as ethylenediaminetetraacetic acid (EDTA). The author concluded that, although much progress had been made, much still remains to be done before a successful and practical solution to this loss of brightness and undesirable yellowing of lignin-containing pulp and/or paper is found.

The instant invention described in detail below provides such a solution where the use of selected hindered amine nitroxides, hindered amine hydroxylamines or their salts in combination with selected UV absorbers and metal chelating agents is seen to prevent loss of brightness and to enhance resistance to yellowing in pulp or paper still containing lignin.

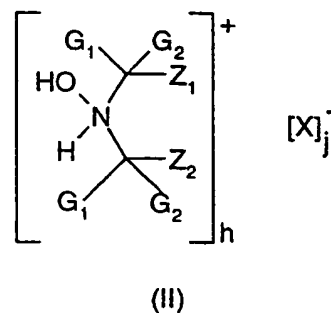
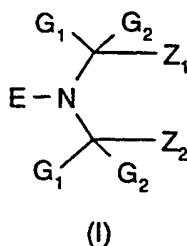
### Detailed Description of the Invention

The addition of hydroxylamines or nitroxide free radicals to high-yield pulp paper either alone or in combinations with UV absorbers, metal chelating agents, fluorescent whitening agents and/or stabilizing polymers effectively achieves light and thermal stability which is similar to that found in papers made from kraft pulps.

Hydroxylamines and nitroxides are known to be efficient free radical traps and may limit the production of o-quinones; UV absorbers limit photochemistry in the underlying substrate to which they are applied, and ultimately reduce the production of free radicals. UV absorbers and nitroxides are each effective at stemming some of the free radical chemistry leading to paper yellowing when used singly. However, when they are used together, hydroxylamines or nitroxides and UV absorbers can effectively stop photochemical yellowing of lignin containing papers which are exposed 24 hours a day under ambient fluorescent lighting conditions for at least 200 days. Both of these types of stabilizers show enhanced inhibiting activity when combined with a metal chelating agent such diethylenetriaminepentaacetic acid, or polymeric inhibitors such as polyethylene glycol.

More particularly the instant invention pertains to a composition having reduced loss of brightness and enhanced resistance to yellowing which comprises

- (a) a pulp or paper which still contains lignin, and
- (b) an effective stabilizing amount of a hindered amine compound of formula I or II



where

G<sub>1</sub> and G<sub>2</sub> are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene,

Z<sub>1</sub> and Z<sub>2</sub> are each methyl, or Z<sub>1</sub> and Z<sub>2</sub> together form a linking moiety which may additionally be substituted by an ester, ether, hydroxy, oxo, cyanohydrin, amide, amino, carboxy or urethane group,

E is oxyl; hydroxyl; hydrogen; alkyl; alkyl substituted by hydroxyl, oxo or carboxy or interrupted by oxygen or carboxy; alkenyl; alkynyl; cycloalkyl; cycloalkenyl; bicycloalkyl; alkoxy; alkoxy substituted by hydroxyl, oxo or carboxy or interrupted by oxygen or carboxy; cycloalkoxy; alkenyloxy; cycloalkenyloxy, aralkyl; aralkoxy; acyl; R'(C=O)O-; R'O(C=O)O-; R'N(C=O)O- or chloro, where R' is an aliphatic or aromatic moiety,

X is an inorganic or organic anion, and

where the total charge of cations h is equal to the total charge of anions j, and with the proviso that the compound of formula I is not bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate or the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid.

Preferably, the compositions are those where in the compound of component (b), E is oxyl, hydroxyl, alkenyloxy, aralkoxy, alkyloxy or alkyl substituted by oxo or interrupted by carboxy, more preferably wherein E is oxyl, hydroxy or alkenyloxy, especially wherein E is oxyl or hydroxy; most especially wherein E is hydroxy.

Specific meanings of E are conveniently as given below for formulas A to EE and A\* to EE\*, as far as they are within the above definitions of E.

Examples for X include X as phosphate, carbonate, bicarbonate, nitrate, chloride, bromide, bisulfite, sulfite, bisulfate, sulfate, borate, carboxylate, an alkylsulfonate or an arylsulfonate, or a phosphonate, like, for example, diethylenetriaminepentamethylenephosphonate. X as carboxylate especially is a carboxylate of a mono-, di-, tri- or tetracarboxylic acid, mainly of 1-18

carbon atoms, such as a formate, acetate, benzoate, citrate, oxalate, tartrate, acrylate, polyacrylate, fumarate, maleate, itaconate, glycolate, gluconate, malate, mandelate, tiglate, ascorbate, polymethacrylate, or of nitrilotriacetic acid, hydroxyethylethylenediaminetriacetic acid, ethylenediaminetetraacetic acid or diethylenetriaminepentaacetic acid.

Most preferably, X is chloride, bisulfite, bisulfate, sulfate, phosphate, nitrate, ascorbate, acetate, citrate or carboxylate of ethylenediaminetetraacetic acid or of diethylenetriaminepentaacetic acid; most especially wherein X is bisulfate or citrate.

h and j are preferably from the range 1-5.

Preferably, Z<sub>1</sub> and Z<sub>2</sub> as a linking moiety are a chain of 2 or 3 carbon atoms or 1 or 2 carbon atoms and a nitrogen or oxygen atom forming together with the remaining structure in formula I or II a saturated 5- or 6-membered heterocyclic ring, which may be substituted as mentioned. The substituents in Z<sub>1</sub> and Z<sub>2</sub> themselves may contain hindered amine moieties. Preferred are compounds of the formula I or II containing 1-4, especially 1 or 2 hindered amine or hindered ammonium moieties. Preferably, Z<sub>1</sub> and Z<sub>2</sub> as a linking moiety is a hydrocarbon containing 1-200, especially 1-60 carbon atoms and 0-60, especially 0-30 heteroatoms selected from oxygen atoms and nitrogen atoms.

Any group denoted as aryl mainly means C<sub>6</sub>-C<sub>12</sub>aryl, preferably phenyl or naphthyl, especially phenyl.

The compounds of component (b) of the invention can be pure or mixtures of compounds.

Groups denoted as alkyl are, within the definitions given, mainly C<sub>1</sub>-C<sub>18</sub>alkyl, for example methyl, ethyl, propyl such as n- or isopropyl, butyl such as n-, iso-, sec- and tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl.

Groups denoted as alkylene are, within the definitions given, for example methylene, 1,2-ethylene, 1,1-ethylene, 1,3-propylene, 1,2-propylene, 1,1-propylene, 2,2-propylene, 1,4-butylene, 1,3-butylene, 1,2-butylene, 1,1-butylene, 2,2-butylene, 2,3-butylene, or -C<sub>5</sub>H<sub>10</sub>-, -



$C_6H_{12}$ -,  $C_7H_{14}$ -,  $-C_8H_{16}$ -,  $-C_9H_{18}$ -,  $-C_{10}H_{20}$ -,  $-C_{11}H_{22}$ -,  $-C_{12}H_{24}$ -,  $-C_{13}H_{26}$ -,  $-C_{14}H_{28}$ -,  $-C_{15}H_{30}$ -,  $-C_{16}H_{32}$ -,  $-C_{17}H_{34}$ -,  $-C_{18}H_{36}$ -.

Groups denoted as cycloalkyl or cycloalkoxy are mainly  $C_5$ - $C_{12}$ cycloalkyl or  $C_5$ - $C_{12}$ cycloalkoxy, the cycloalkyl part being, for example, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl or cyclododecyl. Cycloalkenyl is mainly  $C_5$ - $C_{12}$ cycloalkenyl including cyclopentenyl, cyclohexenyl, cycloheptenyl, cyclooctenyl, cyclononenyl, cyclodecenyl, cycloundecenyl, cyclododecenyl.

Aralkyl or aralkoxy is preferably phenylalkyl or phenylalkoxy, which is alkyl or alkoxy substituted by phenyl. Examples for phenylalkyl or phenylalkoxy are, within the definitions given, benzyl, benzyloxy,  $\alpha$ -methylbenzyl,  $\alpha$ -methylbenzyloxy, cumyl, cumyloxy.

Residues alkenyl, such as in the definition of E or other definitions, are mainly alkenyl of 2 to 18 carbon atoms, most preferably allyl.

Residues alkynyl, such as in the definition of E or other definitions, are mainly alkynyl of 2 to 12 carbon atoms, preferred is propargyl.

A group denoted as acyl is mainly  $R(C=O)$ -, where R is an aliphatic or aromatic moiety.

An aliphatic or aromatic moiety, such as mentioned above or in the definition of E or other definitions, mainly is an aliphatic or aromatic  $C_1$ - $C_{30}$ hydrocarbon; examples are aryl, alkyl, cycloalkyl, alkenyl, cycloalkenyl, bicycloalkyl, bicycloalkenyl, and combinations of these groups.

Examples for acyl groups are alkanoyl of 2 to 12 carbon atoms, alkenoyl of 3 to 12 carbon atoms, benzoyl.

Alkanoyl embraces, for example, formyl, acetyl, propionyl, butyryl, pentanoyl, octanoyl; preferred is  $C_2$ - $C_8$ alkanoyl, especially acetyl.

Residues alkenoyl are most preferably acryloyl or methacryloyl.

The alkyl groups in the different substituents may be linear or branched.

Examples for alkyl of 1 to 6 carbon atoms are methyl ethyl propyl and its isomers, butyl and its isomers pentyl and its isomers and hexyl and its isomers.

Examples for alkenyl groups with 2 to 4 carbon atoms are ethenyl, propenyl, butenyl.

Examples for alkyl groups with 1 to 4 carbon atoms interrupted by one or two oxygen atoms are  $-\text{CH}_2-\text{O}-\text{CH}_3$ ,  $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3$ ,  $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$ ,  $-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3$  or  $-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_3$ .

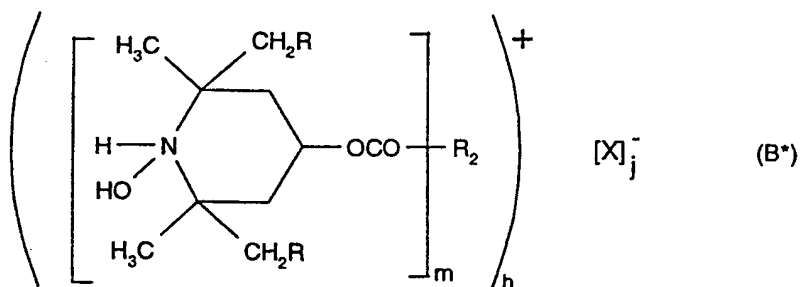
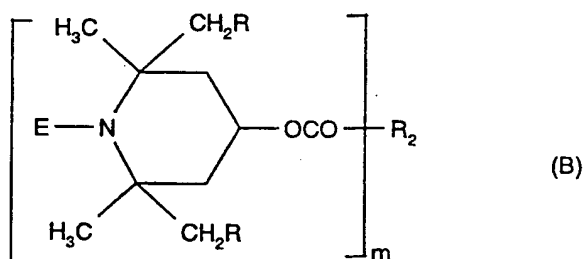
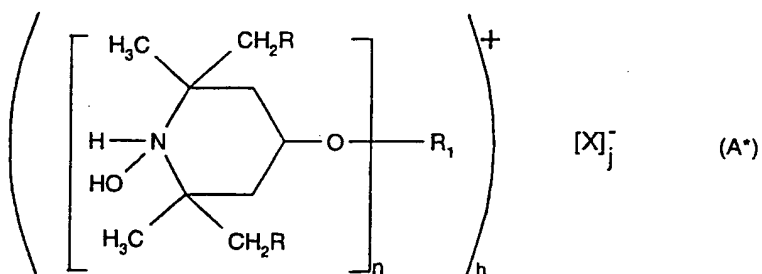
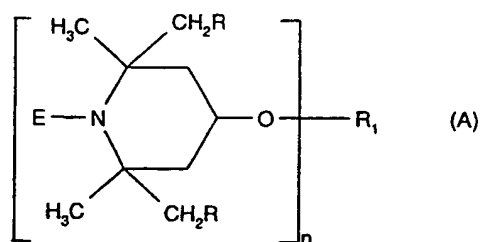
Examples for hydroxy substituted alkyl groups with 2 to 6 carbon atoms are hydroxy ethyl, dihydroxy ethyl, hydroxy propyl, dihydroxy propyl, hydroxy butyl, hydroxy pentyl or hydroxy hexyl.

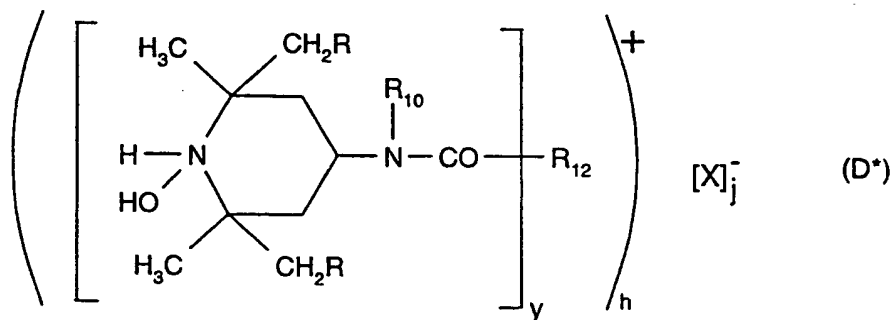
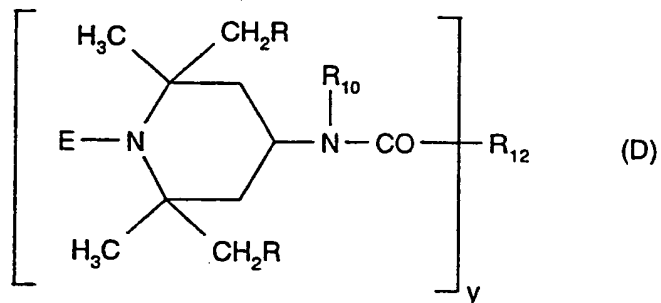
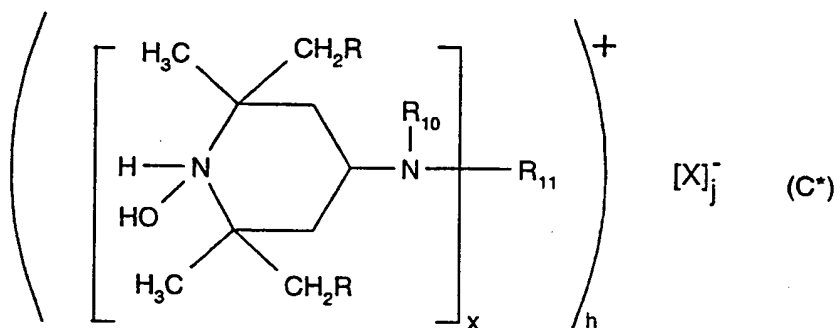
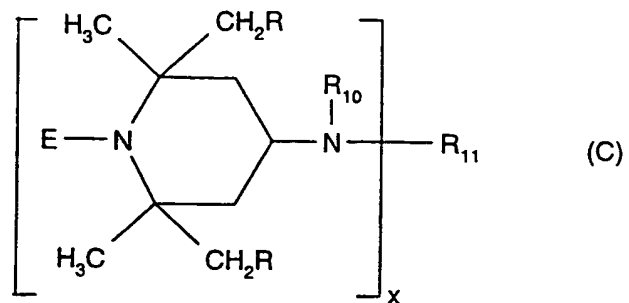
A preferred composition contains a compound of component (b), where E is hydroxyl, alkenyloxy, aralkoxy, alkyloxy substituted by oxo or interrupted by carboxy and X is chloride, bisulfate, sulfate, formate, acetate, benzoate, oxalate, citrate, a carboxylate of ethylenediaminetetraacetic acid or of diethylenetriaminepentaacetic acid or polyacrylate.

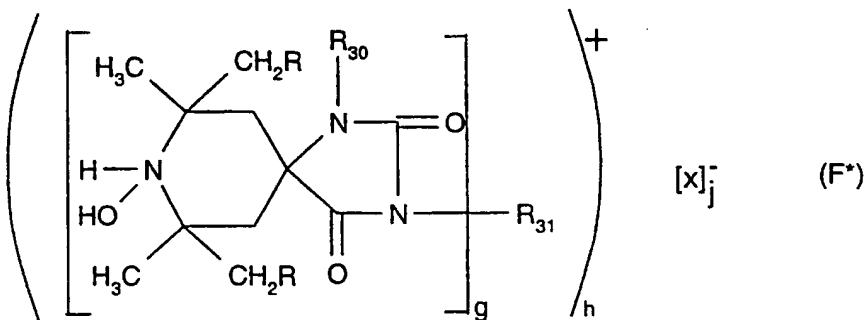
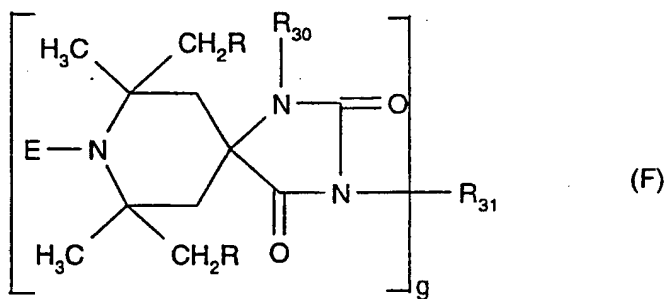
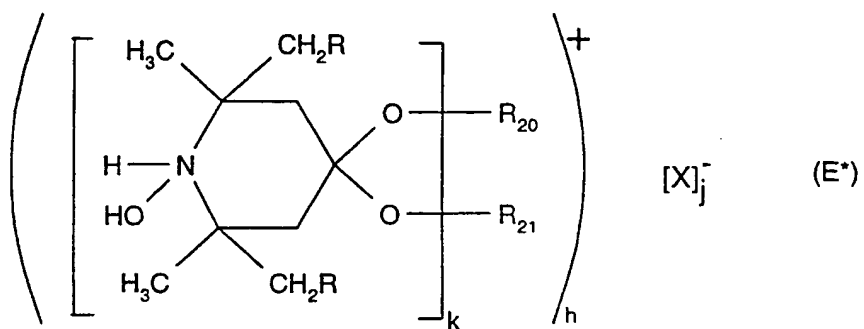
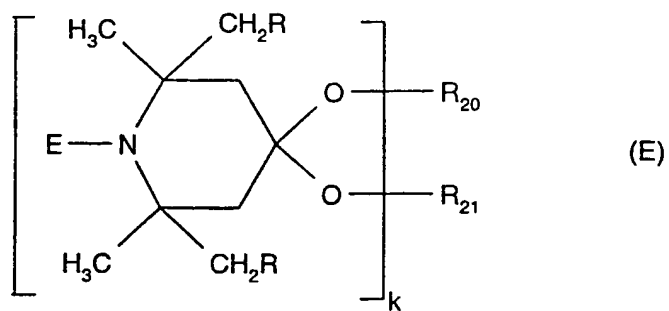
Also preferred is composition where in the compound of component (b), E is hydroxyl or alkenyloxy and X is chloride, bisulfate, sulfate, citrate or a carboxylate of ethylenediaminetetraacetic acid or of diethylenetriaminepentaacetic acid

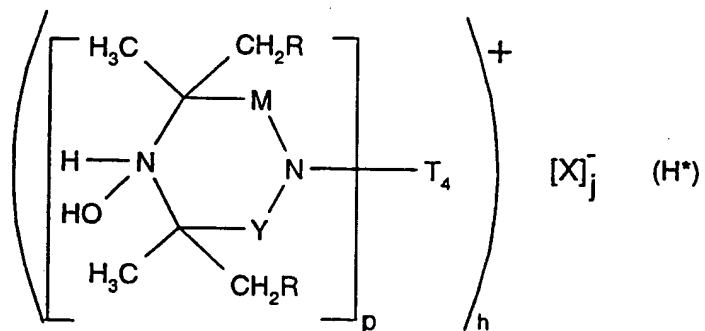
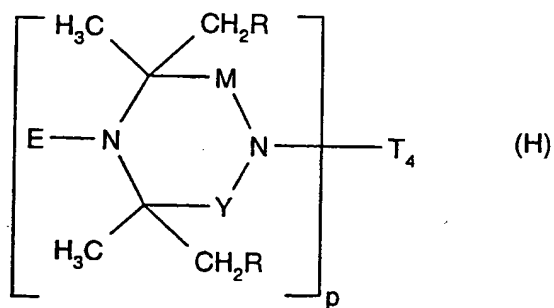
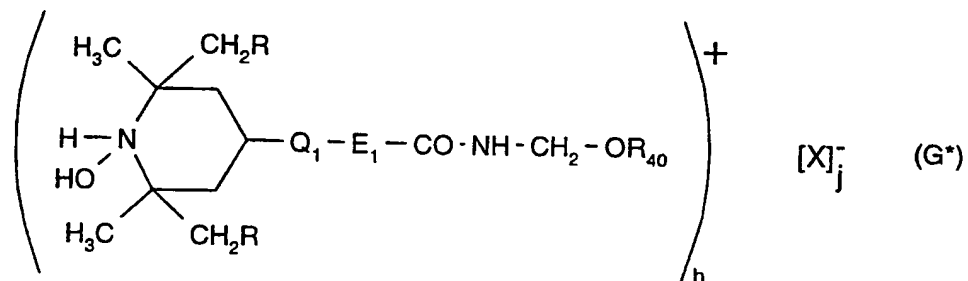
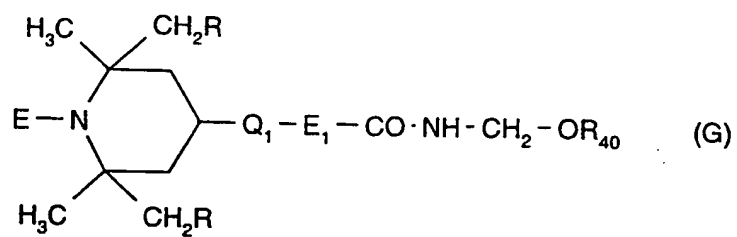
Most preferred is a composition where in the compound of component (b), E is hydroxyl and X is citrate.

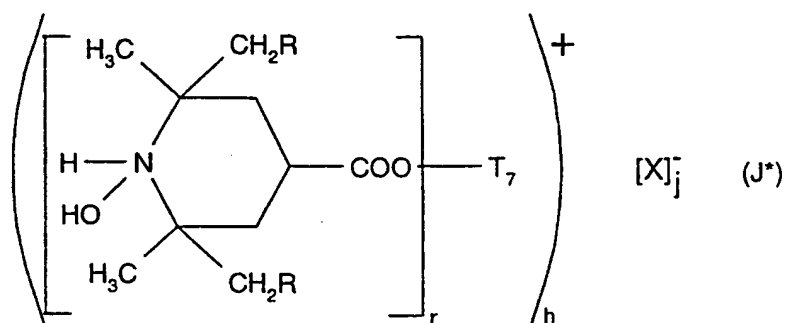
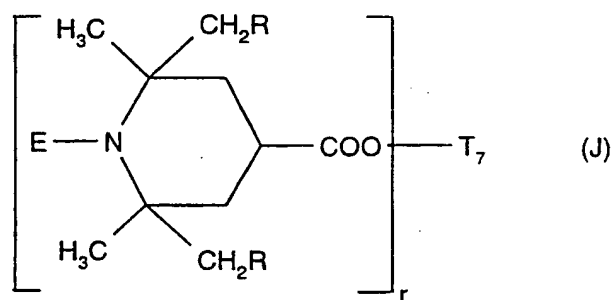
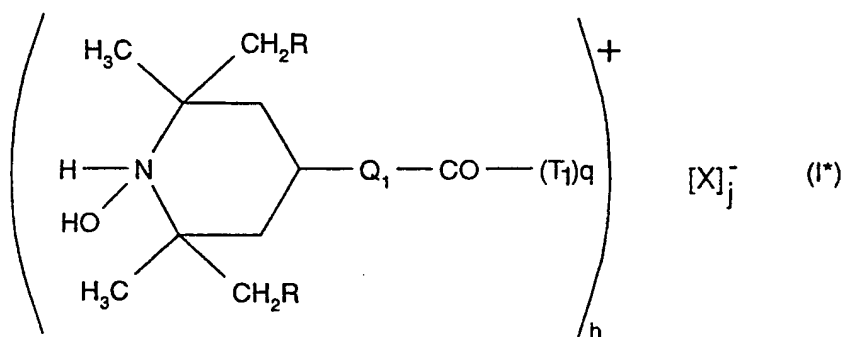
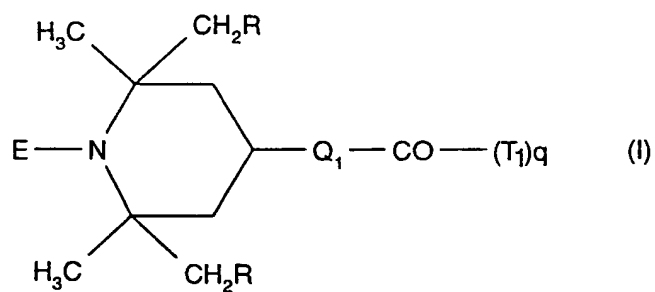
Preferably, the hindered amine compounds of component (b) are those of formulas A to EE and A\* to EE\*

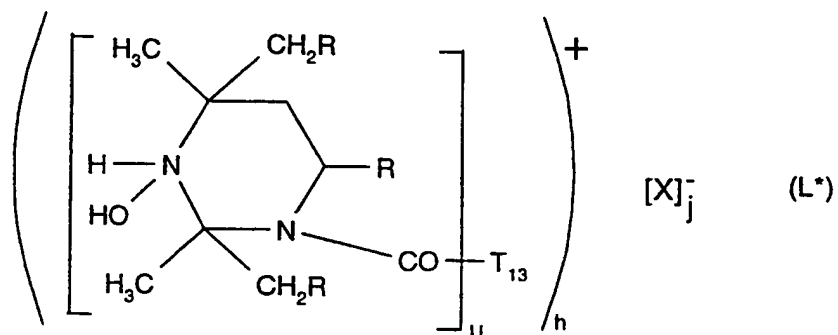
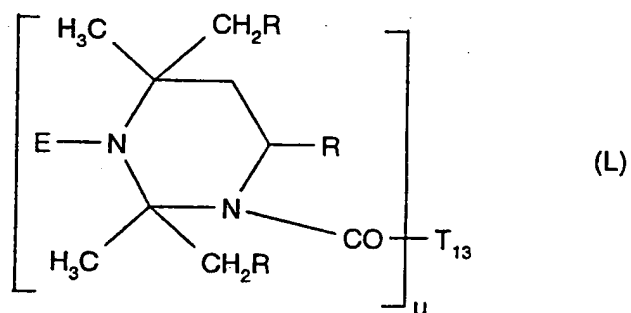
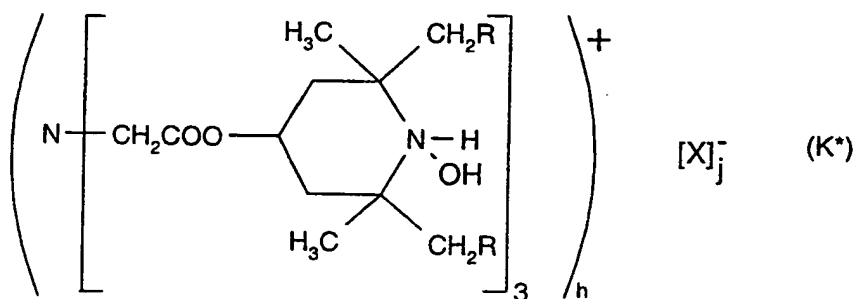
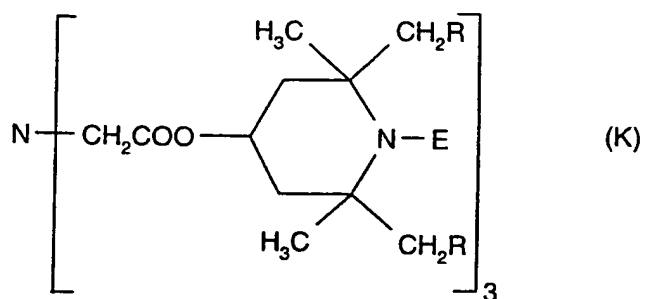




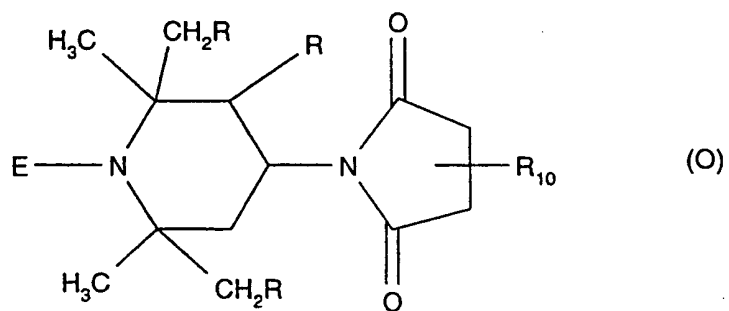
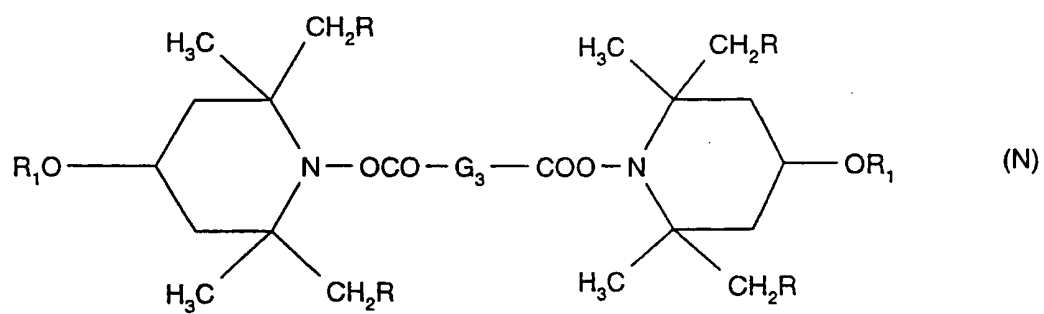
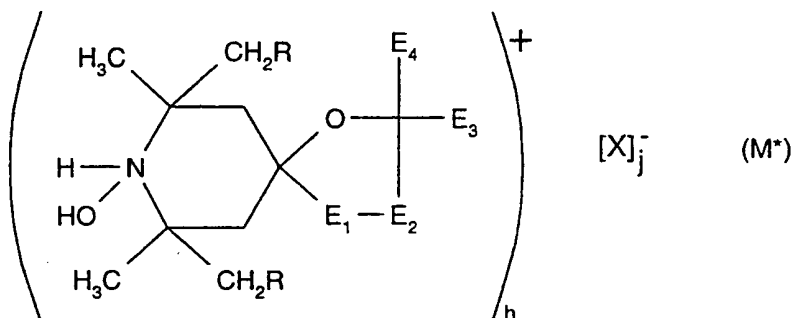
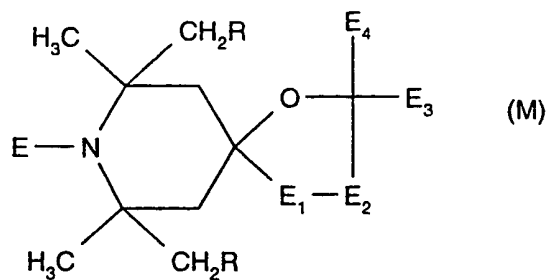


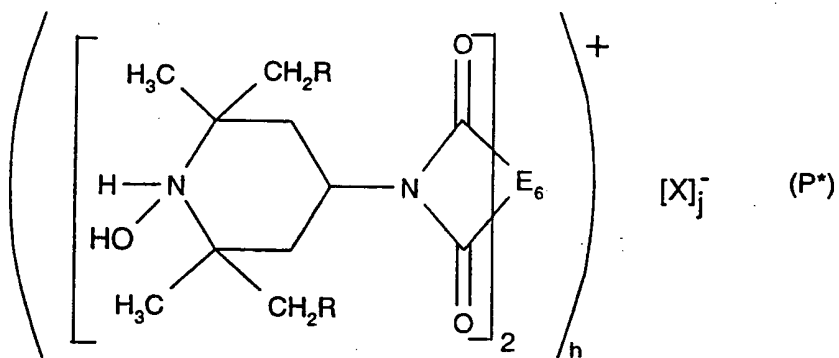
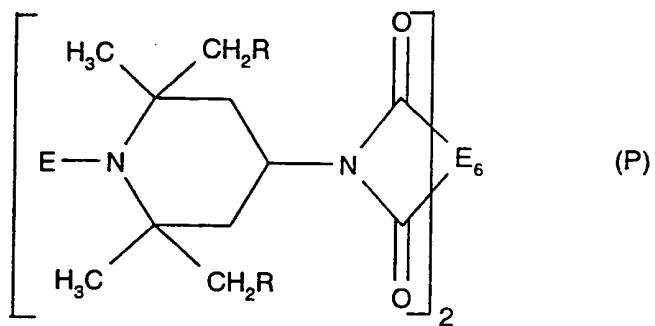
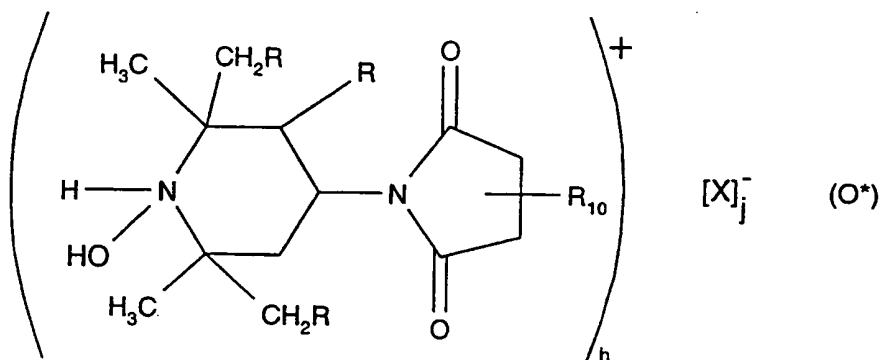


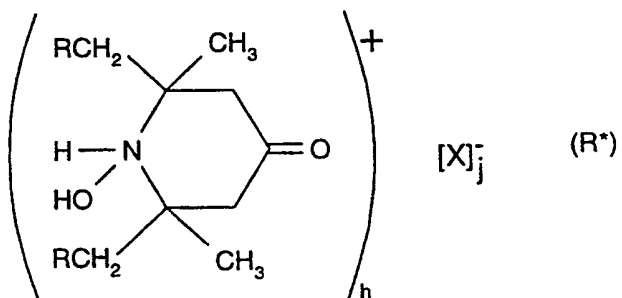
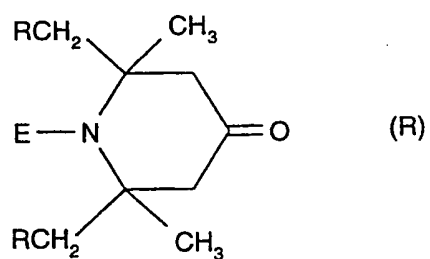
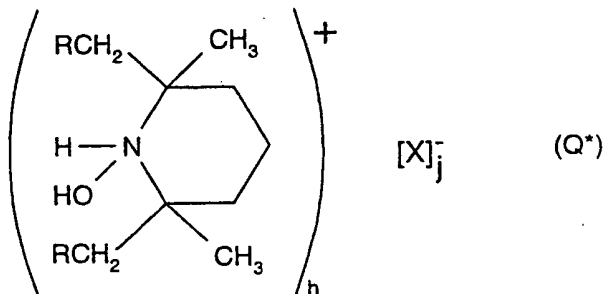
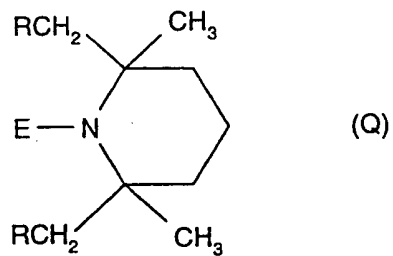


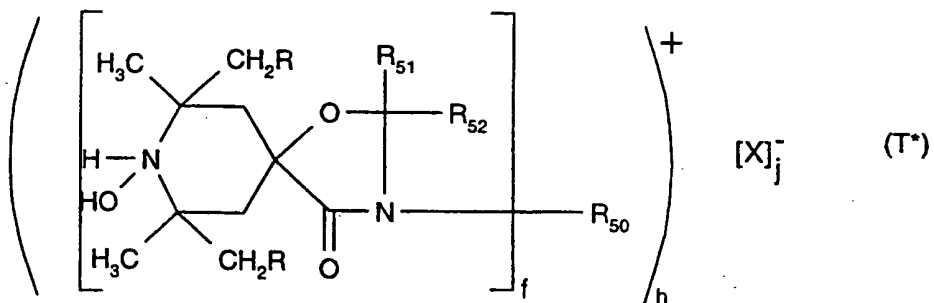
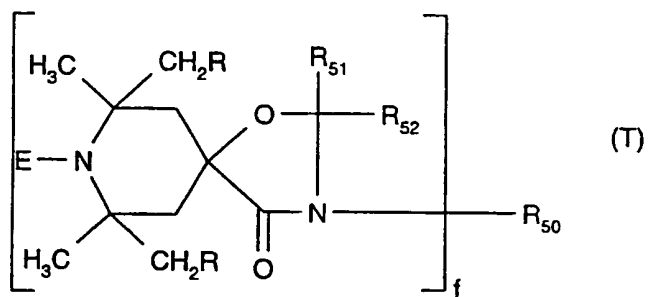
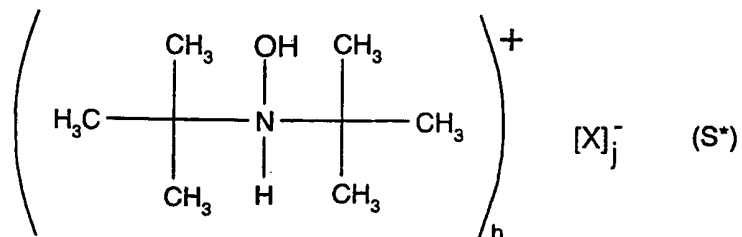
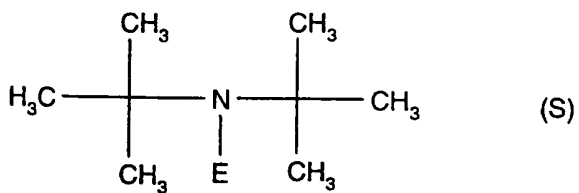


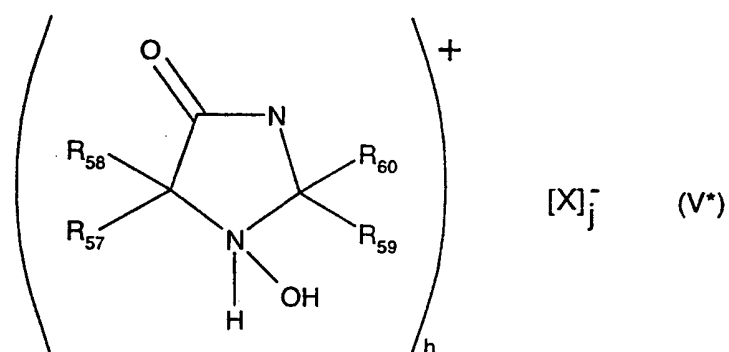
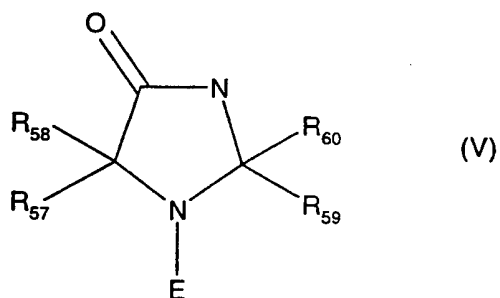
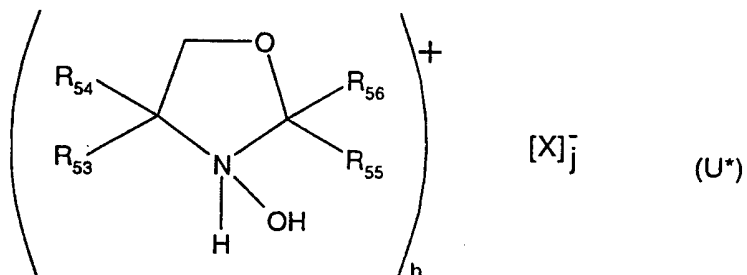
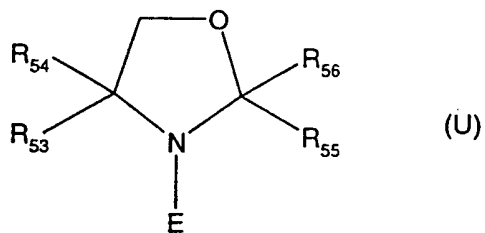


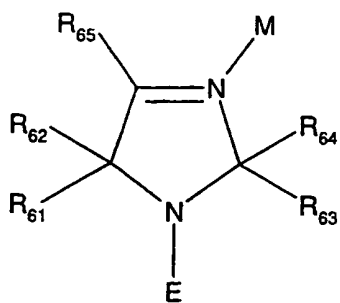




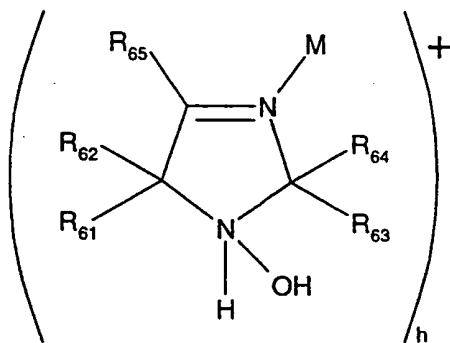






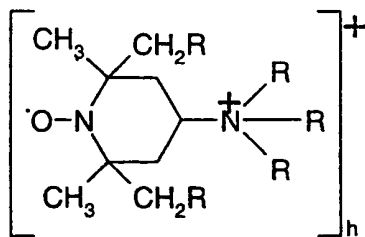


(W)



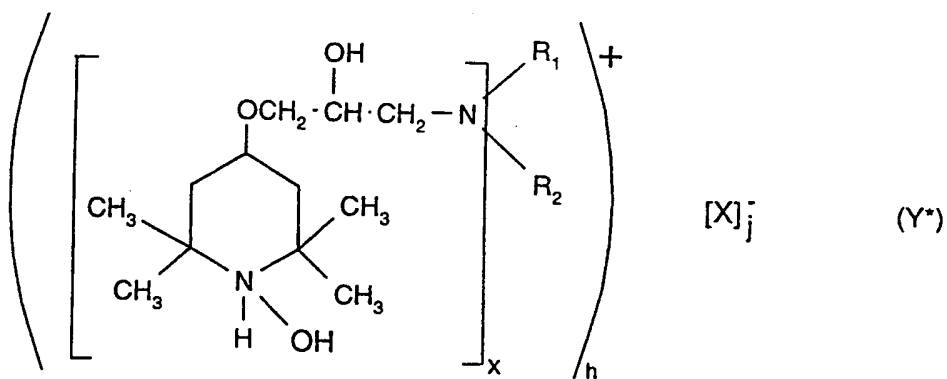
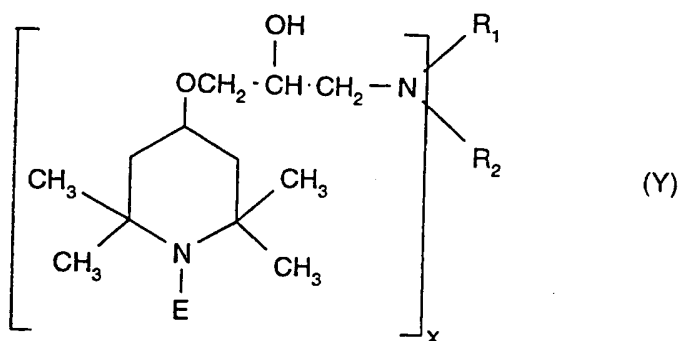
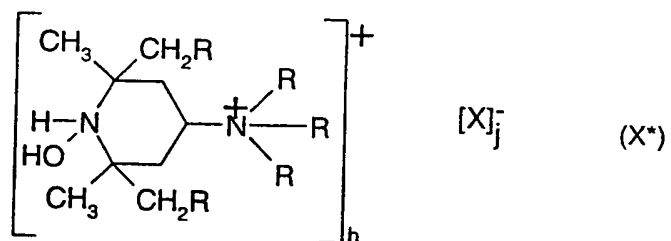
$[X]_j^-$

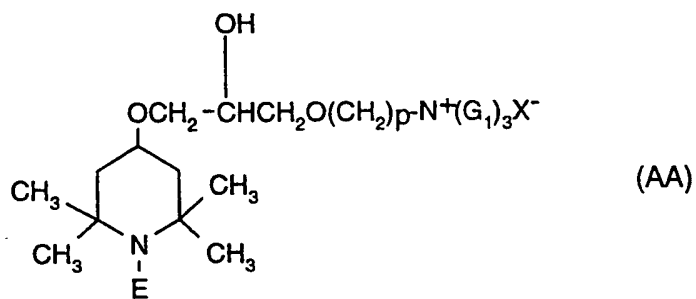
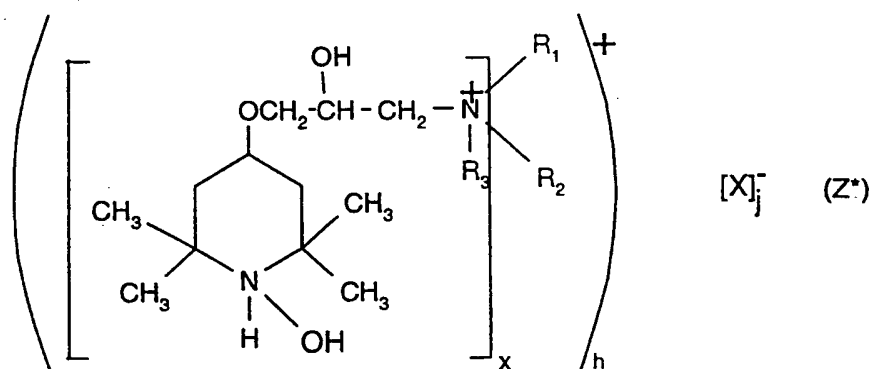
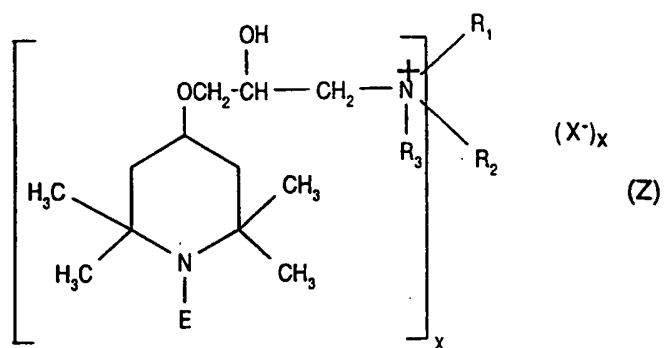
(W\*)



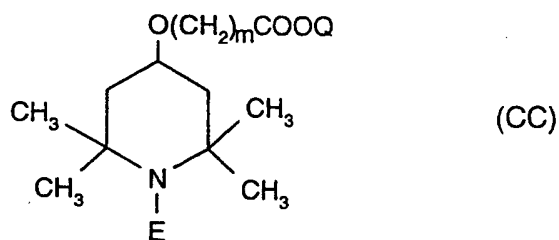
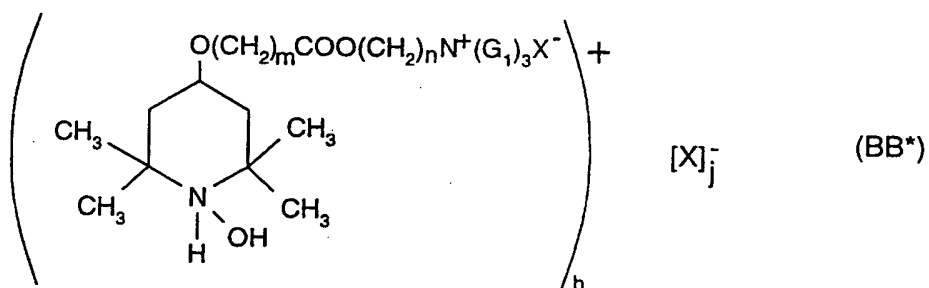
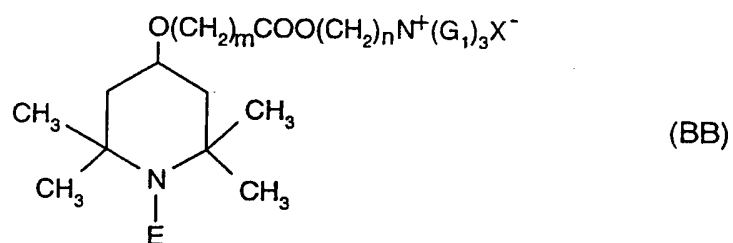
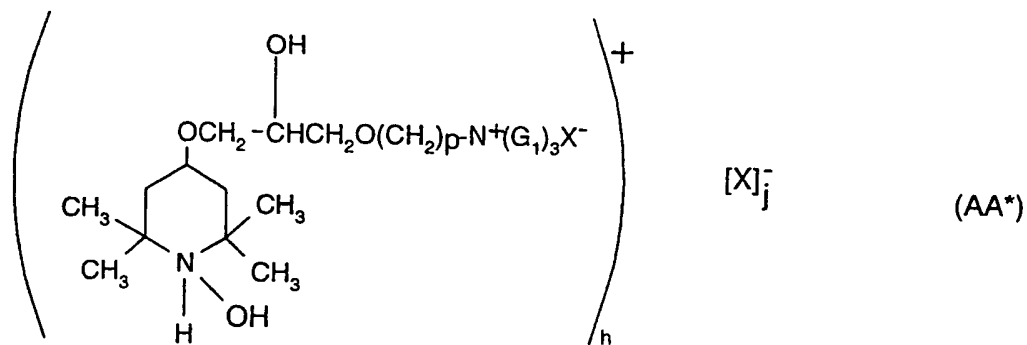
$[X]_j^-$

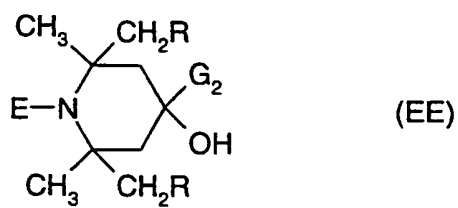
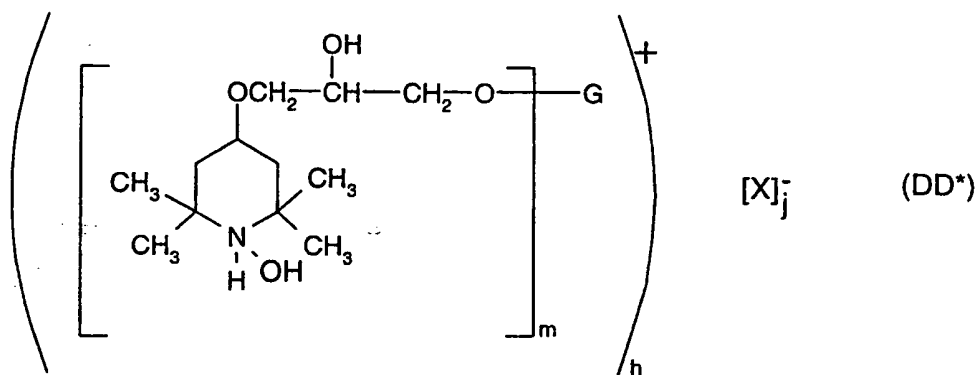
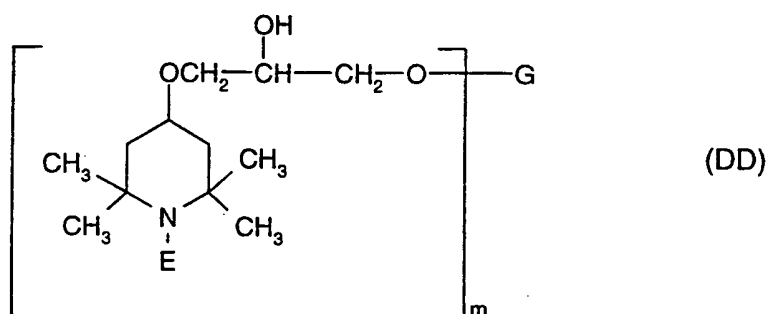
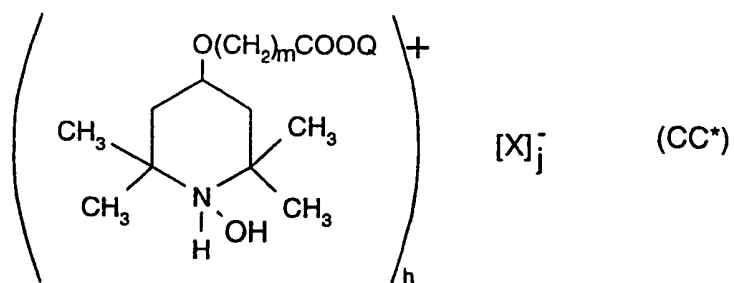
(X)

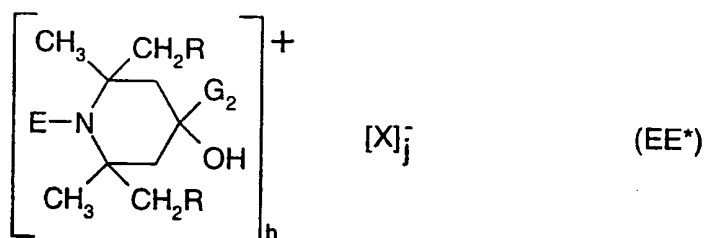












wherein

E is oxyl, hydroxyl, hydrogen, alkyl of 1 to 18 carbon atoms, alkyl of 2 to 12 carbon atoms substituted by one to three hydroxyl or said alkyl interrupted by one to four oxygen atoms, or said alkyl both substituted by said hydroxyl groups and interrupted by said oxygen atoms, alkenyl of 2 to 18 carbon atoms, alkynyl of 2 to 12 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, cycloalkenyl of 5 to 12 carbon atoms, bicycloalkyl of 6 to 10 carbon atoms, alkoxy of 1 to 18 carbon atoms, alkoxy of 2 to 12 carbon atoms substituted by one to three hydroxyl groups or said alkoxy interrupted by one to four oxygen atoms or said alkoxy substituted by -COOZ where Z is hydrogen or alkyl of 1 to 4 carbon atoms, cycloalkoxy of 5 to 12 carbon atoms, cycloalkenyloxy of 5 to 12 carbon atoms, alkenyloxy of 2 to 18 carbon atoms, aralkyl of 7 to 15 carbon atoms, aralkoxy of 7 to 15 carbon atoms, alkanoyl of 2 to 12 carbon atoms, alkenoyl of 3 to 12 carbon atoms, benzoyl, or  $\text{R}'(\text{C}=\text{O})\text{O}-$ ,  $\text{R}'\text{O}(\text{C}=\text{O})\text{O}-$ ,  $\text{R}'\text{N}(\text{C}=\text{O})\text{O}-$ , where  $\text{R}'$  is alkyl of 1 to 6 carbon atoms or phenyl,

R is hydrogen or methyl,

in formula A and A\*,

n is 1 or 2,

when n is 1,

$\text{R}_1$  is hydrogen, alkyl of 1 to 18 carbon atoms, alkenyl of 2-18 carbon atoms, propargyl, glycidyl, alkyl of 2 to 50 carbon atoms interrupted by one to twenty oxygen atoms, said alkyl

substituted by one to ten hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or

$R_1$  is alkyl of 1 to 4 carbon atoms substituted by a carboxy group or by  $-\text{COOZ}$  where Z is hydrogen, alkyl of 1 to 4 carbon atoms or phenyl, or where Z is said alkyl substituted by  $-(\text{COO}^-)_n \text{M}^{n+}$  where n is 1-3 and M is a metal ion from the 1st, 2nd or 3rd group of the periodic table or is Zn, Cu, Ni or Co, or M is a group  $\text{N}^{n+}(\text{R}_2)_4$  where  $\text{R}_2$  is alkyl of 1 to 8 carbon atoms or benzyl,

when n is 2,

$R_1$  is alkylene of 1 to 12 carbon atoms, alkenylene of 4 to 12 carbon atoms, xylylene or alkylene of 1 to 50 carbon atoms interrupted by one to twenty oxygen atoms, substituted by one to ten hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups,

in formula B and B\*,

m is 1 to 4,

when m is 1,

$R_2$  is alkyl of 1 to 18 carbon atoms, alkyl of 3 to 18 carbon atoms interrupted by  $-\text{COO}-$ , alkyl of 3 to 18 carbon atoms substituted by  $\text{COOH}$  or  $\text{COO}^-$ , or  $R_2$  is  $-\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$  where n is 1 to 12, or

$R_2$  is cycloalkyl of 5 to 12 carbon atoms, aryl of 6 to 12 carbon atoms, or said aryl substituted by one to four alkyl groups of 1 to 4 carbon atoms, or

$R_2$  is  $-\text{NHR}_3$  where  $\text{R}_3$  is alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aryl of 6 to 12 carbon atoms, or said aryl substituted by one to four alkyl of 1 to 4 carbon atoms, or

$R_2$  is  $-N(R_3)_2$  where  $R_3$  is as defined above,

when  $m$  is 2,

$R_2$  is alkylene of 1 to 12 carbon atoms, alkenylene of 4 to 12 carbon atoms, xylylene, alkylene of 2 to 12 carbon atoms interrupted by  $-COO-$ , alkylene of 3 to 18 carbon atoms substituted by  $COOH$  or  $COO-$ , or  $R_2$  is  $-CH_2(OCH_2CH_2)_nOCH_2-$  where  $n$  is 1 to 12, or

$R_2$  is cycloalkylene of 5 to 12 carbon atoms, aralkylene of 7 to 15 carbon atoms or arylene of 6 to 12 carbon atoms, or

$R_2$  is  $-NHR_4NH-$  where  $R_4$  is alkylene of 2 to 18 carbon atoms, cycloalkylene of 5 to 12 carbon atoms, aralkylene of 8 to 15 carbon atoms or arylene of 6 to 12 carbon atoms, or

$R_2$  is  $-N(R_3)R_4N(R_3)-$  where  $R_3$  and  $R_4$  are as defined above, or

$R_2$  is  $-CO-$  or  $-NH-CO-NH-$ ,

when  $m$  is 3,

$R_2$  is alkanetriyl of 3 to 8 carbon atoms or benzenetriyl, or

when  $m$  is 4,

$R_2$  is alkanetetrayl of 5 to 8 carbon atoms or benzenetetrayl,

in formula C and C\*,

$R_{10}$  is hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, alkanoyl of 2 to 18 carbon atoms, alkenoyl of 3 to 5 carbon atoms or benzoyl,

x is 1 or 2,

when x is 1,

$R_{11}$  is hydrogen, alkyl of 1 to 18 carbon atoms, alkenyl of 2 to 18 carbon atoms, propargyl, glycidyl, alkyl of 2 to 50 carbon atoms interrupted by one to twenty oxygen atoms, said alkyl substituted by one to ten hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or

$R_{11}$  is alkyl of 1 to 4 carbon atoms substituted by a carboxy group or by  $-\text{COOZ}$  where Z is hydrogen, alkyl of 1 to 4 carbon atoms or phenyl, or where Z is said alkyl substituted by  $-(\text{COO}^-)_n \text{M}^{n+}$  where n is 1-3 and M is a metal ion from the 1st, 2nd or 3rd group of the periodic table or is Zn, Cu, Ni or Co, or M is a group  $\text{N}^{n+}(\text{R}_2)_4$  where  $\text{R}_2$  is hydrogen, alkyl of 1 to 8 carbon atoms or benzyl, or

when x is 2,

$R_{11}$  is alkylene of 1 to 12 carbon atoms, alkenylene of 4 to 12 carbon atoms, xylylene or alkylene of 1 to 50 carbon atoms interrupted by one to twenty oxygen atoms, substituted by one to ten hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups,

in formula D and D\*,

$R_{10}$  is as defined above,

y is 1 to 4, and

$R_{12}$  is defined as  $R_2$  above,

in formula E and E\*,

k is 1 or 2,

when k is 1,

$R_{20}$  and  $R_{21}$  are independently alkyl of 1 to 12 carbon atoms, alkenyl of 2 to 12 carbon atoms or aralkyl of 7 to 15 carbon atoms, or  $R_{20}$  is also hydrogen, or

$R_{20}$  and  $R_{21}$  together are alkylene of 2 to 8 carbon atoms or said alkylene substituted by hydroxyl, or are acyloxy-alkylene of 4 to 22 carbon atoms, or

when k is 2,

$R_{20}$  and  $R_{21}$  are together  $(-CH_2)_2C(CH_2-)_2$ ,

in formula F and F\*,

$R_{30}$  is hydrogen, alkyl of 1 to 18 carbon atoms, benzyl, glycidyl, or alkoxyalkyl of 2 to 6 carbon atoms,

g is 1 or 2,

when g is 1,  $R_{31}$  is defined as  $R_1$  above when n is 1,

when g is 2,  $R_{31}$  is defined as  $R_1$  above when n is 2,

in formula G and G\*,

$Q_1$  is  $-NR_{41}-$  or  $-O-$ ,

$E_1$  is alkylene of 1 to 3 carbon atoms, or  $E_1$  is  $-CH_2-CH(R_{42})-O-$  where  $R_{42}$  is hydrogen, methyl or phenyl, or  $E_1$  is  $-(CH_2)_3-NH-$  or  $E_1$  is a direct bond,

$R_{40}$  is hydrogen or alkyl of 1 to 18 carbon atoms,

$R_{41}$  is hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms, or  $R_{41}$  is  $-\text{CH}_2-\text{CH}(\text{R}_{42})-\text{OH}$  where  $\text{R}_{42}$  is as defined above,

in formula H and  $\text{H}^*$ ,

$p$  is 1 or 2,

$\text{T}_4$  is as defined for  $\text{R}_{11}$  when  $x$  is 1 or 2,

$\text{M}$  and  $\text{Y}$  are independently methylene or carbonyl, preferably  $\text{M}$  is methylene and  $\text{Y}$  is carbonyl,

in formula I and  $\text{I}^*$ ,

this formula denotes a recurring structural unit of a polymer where  $\text{T}_1$  is ethylene or 1,2-propylene or is the repeating structural unit derived from an alpha-olefin copolymer with an alkyl acrylate or methacrylate, and where

$q$  is 2 to 100,

$\text{Q}_1$  is  $-\text{N}(\text{R}_{41})-$  or  $-\text{O}-$  where  $\text{R}_{41}$  is as defined above,

in formula J and  $\text{J}^*$ ,

$r$  is 1 or 2,

$\text{T}_7$  is as defined for  $\text{R}_1$  when  $n$  is 1 or 2 in formula A,

preferably  $\text{T}_7$  is octamethylene when  $r$  is 2,



in formula L and L\*,

u is 1 or 2,

T<sub>13</sub> is as defined for R<sub>1</sub> when n is 1 or 2 in formula A, with the proviso that T<sub>13</sub> is not hydrogen when u is 1,

in formula M and M\*,

E<sub>1</sub> and E<sub>2</sub>, being different, each are -CO- or -N(E<sub>5</sub>)- where E<sub>5</sub> is hydrogen, alkyl of 1 to 12 carbon atoms or alkoxycarbonylalkyl of 4 to 22 carbon atoms, preferably E<sub>1</sub> is -CO- and E<sub>2</sub> is -N(E<sub>5</sub>)-,

E<sub>3</sub> is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl, said phenyl or said naphthyl substituted by chlorine or by alkyl of 1 to 4 carbon atoms, or phenylalkyl of 7 to 12 carbon atoms, or said phenylalkyl substituted by alkyl of 1 to 4 carbon atoms,

E<sub>4</sub> is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl or phenylalkyl of 7 to 12 carbon atoms, or

E<sub>3</sub> and E<sub>4</sub> together are polymethylene of 4 to 17 carbon atoms, or said polymethylene substituted by one to four alkyl of 1 to 4 carbon atoms, preferably methyl,

in formula N and N\*,

R<sub>1</sub> is as defined for R<sub>1</sub> in formula A when n is 1,

G<sub>3</sub> is a direct bond, alkylene of 1 to 12 carbon atoms, phenylene or -NH-G<sub>1</sub>-NH- where G<sub>1</sub> is alkylene of 1 to 12 carbon atoms,

in formula O and O\*,

$R_{10}$  is as defined for  $R_{10}$  in formula C,

in formula P and P\*,

$E_6$  is an aliphatic or aromatic tetravalent radical, preferably neopentantetrayl or benzenetetrayl,

in formula T and T\*,

$R_{51}$  is hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, or aryl of 6 to 10 carbon atoms,

$R_{52}$  is hydrogen or alkyl of 1 to 18 carbon atoms, or

$R_{51}$  and  $R_{52}$  together of alkylene of 4 to 8 carbon atoms,

f is 1 or 2,

when f is 1,

$R_{50}$  is as defined for  $R_{11}$  in formula C when x is 1, or  $R_{50}$  is  $-(CH_2)_zCOOR_{54}$  where z is 1 to 4 and  $R_{54}$  is hydrogen or alkyl of 1 to 18 carbon atoms, or  $R_{54}$  is a metal ion from the 1st, 2nd or 3rd group of the periodic table or a group  $-N(R_{55})_4$  where  $R_{55}$  is hydrogen, alkyl of 1 to 12 carbon atoms or benzyl,

when f is 2,  $R_{50}$  is as defined for  $R_{11}$  in formula C when x is 2,

in formula U and U\*,

$R_{53}$ ,  $R_{54}$ ,  $R_{55}$  and  $R_{56}$  are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene.

in formula V and V\*,

R<sub>57</sub>, R<sub>58</sub>, R<sub>59</sub> and R<sub>60</sub> are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene.

in formula W and W\*,

R<sub>61</sub>, R<sub>62</sub>, R<sub>63</sub> and R<sub>64</sub> are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene,

R<sub>65</sub> is alkyl of 1 to 5 carbon atoms,

M is hydrogen or oxygen,

wherein in formulas X to CC and X\* to CC\*

n is 2 to 3,

G<sub>1</sub> is hydrogen, methyl, ethyl, butyl or benzyl,

m is 1 to 4,

x is 1 to 4,

when x is 1, R<sub>1</sub> and R<sub>2</sub> are independently alkyl of 1 to 18 carbon atoms, said alkyl interrupted by one to five oxygen atoms, said alkyl substituted by 1 to 5 hydroxyl groups or said alkyl both interrupted by said oxygen atoms and substituted by said hydroxyl groups; cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one to three alkyl of 1 to 8 carbon atoms, or R<sub>1</sub> is also hydrogen,

or R<sub>1</sub> and R<sub>2</sub> are together tetramethylene, pentamethylene, hexamethylene or 3-oxapentamethylene,

when x is 2,

$R_1$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or said alkyl both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

$R_2$  is alkylene of 2 to 18 carbon atoms, said alkylene interrupted by one to five oxygen atoms, said alkylene substituted by 1 to 5 hydroxyl groups or said alkylene both interrupted by said oxygen atoms and substituted by said hydroxyl groups; o-, m- or p-phenylene or said phenylene substituted by one or two alkyl of 1 to 4 carbon atoms, or

$R_2$  is  $-(CH_2)_kO[(CH_2)_kO]_h(CH_2)_k-$  where k is 2 to 4 and h is 1 to 40, or

$R_1$  and  $R_2$  together with the two N atoms to which they are attached are piperazin-1,4-diyl,

when x is 3,

$R_1$  is hydrogen,

$R_2$  is alkylene of 4 to 8 carbon atoms interrupted by one nitrogen atom,

when x is 4,

$R_1$  is hydrogen,

$R_2$  is alkylene of 6 to 12 carbon atoms interrupted by two nitrogen atoms,

$R_3$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

p is 2 or 3, and

Q is an alkali metal salt, ammonium or  $N^+(G_1)_4$ ,

in formula DD and DD\*

m is 2 or 3,

when m is 2, G is  $-(CH_2CHR-O)_rCH_2CHR-$ , where r is 0 to 3, and R is hydrogen or methyl, and

when m is 3, G is glyceryl,

in formula EE and EE\*

$G_2$  is  $-CN$ ,  $-CONH_2$  or  $-COOG_3$  where  $G_3$  is hydrogen, alkyl of 1 to 18 carbon atoms or phenyl,

X is an inorganic or organic anion, such as phosphate, phosphonate, carbonate, bicarbonate, nitrate, chloride, bromide, bisulfite, sulfite, bisulfate, sulfate, borate, formate, acetate, benzoate, citrate, oxalate, tartrate, acrylate, polyacrylate, fumarate, maleate, itaconate, glycolate, gluconate, malate, mandelate, tiglate, ascorbate, polymethacrylate, a carboxylate of nitrilotriacetic acid, hydroxyethylethylenediaminetriacetic acid, ethylenediaminetetraacetic acid or of diethylenetriaminepentaacetic acid, a diethylenetriaminepentamethylenephosphonate, an alkylsulfonate or an arylsulfonate, and

where the total charge of cations h is equal to the total charge of anions j, and with the proviso that bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate or the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid are excluded.

Most preferably, the compounds of component (b) are those of formulas A, A\*, B, B\*, C, C\*, D, D\*, Q, Q\*, R, R\*, S, S\*, X, X\*, Y, Y\*, Z and Z\*,

where E is oxyl or hydroxyl,

R is hydrogen,

in formula A and A\*

n is 1 or 2,

when n is 1,

R<sub>1</sub> is hydrogen, alkyl of 1 to 6 carbon atoms, alkenyl of 2-6 carbon atoms, propargyl, glycidyl, alkyl of 2 to 20 carbon atoms interrupted by one to ten oxygen atoms, said alkyl substituted by one to five hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or

R<sub>1</sub> is alkyl of 1 to 4 carbon atoms substituted by a carboxy group or by -COOZ where Z is hydrogen or alkyl of 1 to 4 carbon atoms,

when n is 2,

R<sub>1</sub> is alkylene of 1 to 8 carbon atoms, alkenylene of 4 to 8 carbon atoms, alkylene of 1 to 20 carbon atoms interrupted by one to ten oxygen atoms, substituted by one to five hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups,

in formula B and B\*

m is 1 or 2

when m is 1,

R<sub>2</sub> is alkyl of 1 to 4 carbon atoms or R<sub>2</sub> is CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub> where n is 1 to 12, or

$R_2$  is phenyl, or said phenyl substituted by one to three methyl groups,

$R_2$  is  $-NHR_3$  where  $R_3$  is alkyl of 1 to 4 carbon atoms or phenyl, or said phenyl substituted by one or two methyl groups,

when  $m$  is 2,

$R_2$  is alkylene of 1 to 8 carbon atoms, alkenylene of 4 to 8 carbon atoms, or  $R_2$  is  $-CH_2(OCH_2CH_2)_nOCH_2-$  where  $n$  is 1 to 12, or

$R_2$  is  $NHR_4NH$  where  $R_4$  is of 2 to 6 carbon atoms, aralkylene of 8 to 15 carbon atoms or arylene of 6 to 12 carbon atoms, or

$R_2$  is  $-CO-$  or  $-NHCONH-$ ,

in formula C and C\*,

$R_{10}$  is hydrogen or, alkanoyl of 1 to 3 carbon atoms,

$x$  is 1 or 2,

when  $x$  is 1,

$R_{11}$  is hydrogen, alkyl of 1 to 6 carbon atoms or glycidyl,

$R_{11}$  is alkyl of 1 to 4 carbon atoms substituted by a carboxy group or by  $COOZ$  where  $Z$  is hydrogen or alkyl of 1 to 4 carbon atoms,

when  $x$  is 2,

$R_{11}$  is alkylene of 1 to 6 carbon atoms,

in formula D and D\*,

$R_{10}$  is hydrogen,

y is 1 or 2,

$R_{12}$  is defined as  $R_2$  above,

in formula Y, Y\*, Z and Z\*,

x is 1 or 2,

when x is 1,

$R_1$  and  $R_2$  are independently alkyl of 1 to 4 carbon atoms,

or  $R_1$  and  $R_2$  are together tetramethylene, or pentamethylene,

$R_2$  is hydrogen or alkyl of 1 to 4 carbon atoms, said alkyl group substituted by a hydroxyl group,

when x is 2,

$R_1$  is hydrogen, alkyl of 1 to 4 carbon atoms, said alkyl substituted by a hydroxyl group,

$R_2$  is alkylene of 2 to 6 carbon atoms,

$R_3$  is as defined above.

Especially preferred, the compounds of component (b) are those of formulas A, A\*, B, B\*, C, C\*, D, D\*, Q, Q\*, R and R\*.



where E is oxyl or hydroxyl,

R is hydrogen,

in formula A and A\*,

h is 1,

R<sub>1</sub> is hydrogen, alkyl of 1 to 4 carbon atoms, glycidyl, alkyl of 2 to 4 carbon atoms interrupted by one or two oxygen atoms, said alkyl substituted by one or two hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or

R<sub>1</sub> is alkyl of 1 to 4 carbon atoms substituted by -COOZ where Z is hydrogen or alkyl of 1 to 4 carbon atoms,

in formula B and B\*,

m is 1 or 2,

R<sub>2</sub> is alkyl of 1 to 4 carbon atoms or R<sub>2</sub> is CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub> where n is 1 to 4,

when m is 2,

R<sub>2</sub> is alkylene of 1 to 8 carbon atoms,

in formula C and C\*,

R<sub>10</sub> is hydrogen or alkanoyl of 1 or 2 carbon atoms,

x is 1 or 2,

when x is 1,

$R_{11}$  is hydrogen, alkyl of 1 to 4 carbon atoms or glycidyl,

$R_{11}$  is alkyl of 1 to 4 carbon atoms substituted by COOZ where Z is hydrogen or alkyl of 1 to 4 carbon atoms,

when x is 2,

$R_{11}$  is alkylene of 1 to 6 carbon atoms,

in formula D and D\*,

$R_{10}$  is hydrogen,

y is 1 or 2,

$R_{12}$  is defined as  $R_2$  above.

More particularly, the hindered amine compound is

- (a) bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
- (b) bis(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
- (c) 1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium citrate;
- (d) 1-oxyl-2,2,6,6-tetramethyl-4-acetamidopiperidine;
- (e) 1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidine;
- (f) 1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium bisulfate;
- (g) 1-oxyl-2,2,6,6-tetramethyl-4-oxo-piperidine;
- (h) 1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidine;
- (i) 1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium acetate;
- (j) 1-oxyl-2,2,6,6-tetramethyl-4-methoxy-piperidine;

- (k) 1-hydroxy-2,2,6,6-tetramethyl-4-methoxy-piperidine;
- (l) 1-hydroxyl-2,2,6,6-tetramethyl-4-methoxy-piperidinium acetate;
- (m) 1-oxyl-2,2,6,6-tetramethyl-4-acetoxypiperidine;
- (n) 1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidine;
- (o) 1-oxyl-2,2,6,6-tetramethyl-4-propoxy-piperidine;
- (p) 1-hydroxy-2,2,6,6-tetramethyl-4-propoxy-piperidinium acetate;
- (q) 1-hydroxy-2,2,6,6-tetramethyl-4-propoxy-piperidine;
- (r) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxypiperidine);
- (s) 1-hydroxy-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxypiperidinium acetate);
- (t) 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine;
- (u) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidine;
- (v) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium chloride;
- (w) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium acetate;
- (x) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium bisulfate;
- (y) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium citrate;
- (z) bis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) citrate;
- (aa) tris(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) citrate.
- (bb) tetra(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) ethylenediaminetetraacetate;
- (cc) tetra(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) ethylenediaminetetraacetate;
- (dd) tetra(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium) ethylenediaminetetraacetate;
- (ee) penta(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) diethylenetriaminepentaacetate;
- (ff) penta(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) diethylenetriaminepentaacetate;
- (gg) penta(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium) diethylenetriaminepentaacetate;
- (hh) tri(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) nitrilotriacetate;
- (ii) tri(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) nitrilotriacetate;
- (jj) tri(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium) nitrilotriacetate;

- (kk) penta(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium)  
diethylenetriaminepentamethylenephosphonate;
- (ll) penta(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium)  
diethylenetriaminepentamethylenephosphonate;
- (mm) penta(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium)  
diethylenetriaminepentamethylenephosphonate.

Most especially, the hindered amine compound is

- (a) 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine;
- (b) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidine;
- (c) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium chloride;
- (d) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium acetate;
- (e) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium bisulfate;
- (f) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium citrate;
- (g) bis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) citrate;
- (h) tris(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) citrate;
- (i) tetra(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium)  
ethylenediaminetetraacetate;
- (j) tetra(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium)  
ethylenediaminetetraacetate;
- (k) tetra(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium) ethylenediaminetetraacetate;
- (l) penta(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium)  
diethylenetriaminepentaacetate;
- (m) penta(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium)  
diethylenetriaminepentaacetate;
- (n) penta(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium)  
diethylenetriaminepentaacetate.

The instant compositions may additionally include an effective stabilizing amount of at least one coadditive selected from the group consisting of the UV absorbers, the polymeric

inhibitors, the sulfur containing inhibitors, the phosphorus containing compounds, the nitrones, the benzofuran-2-ones and the hydroxylamines and mixtures thereof.

The compositions which also include a UV absorber are especially preferred. The UV absorber is selected from group consisting of the benzotriazoles, the s-triazines, the benzophenones, the  $\alpha$ -cyanoacrylates, the oxanilides, the benzoxazinones, the benzoates and the  $\alpha$ -alkyl cinnamates.

Preferably, the UV absorber is a benzotriazole, an s-triazine or a benzophenone, most especially a benzotriazole UV absorber or benzophenone UV absorber.

The amount of the coadditive preferably is 0.001 to 5%, more preferably from 0.005 to 2%, especially from 0.01 to 2% by weight based on the pulp or paper.

Typical compositions of the invention are those wherein

- the additional coadditive is a UV absorber, which is preferably selected from group consisting of the benzotriazoles, the s-triazines, the benzophenones, the  $\alpha$ -cyanoacrylates, the oxanilides, the benzoxazinones, the benzoates and the  $\alpha$ -alkyl cinnamates, especially the benzotriazoles, s-triazines and benzophenones;
- the additional coadditive is a polymeric inhibitor, which is preferably poly(ethylene glycol), poly(propylene glycol), poly(butylene glycol), poly(vinyl pyrrolidone or poly(ethylene/propylene glycol);
- the additional coadditive is a fluorescent whitening agent, preferably selected from the group consisting of the 4,4'-bis-(triazinylamino)-stilbene-2,2'-disulfonic acids, 4,4'-bis-(triazol-2-yl)stilbene-2,2'-disulfonic acids, 4,4'-dibenzofuranyl-biphenyls, 4,4'-(diphenyl)-stilbenes, 4,4'-distyryl-biphenyls, 4-phenyl-4'-benzoxazolyl-stilbenes, stilbenyl-naphthotriazoles, 4-styryl-stilbenes, bis-(benzoxazol-2-yl) derivatives, bis-(benzimidazol-2-yl) derivatives, coumarins, pyrazolines, naphthalimides, triazinyl-pyrenes, 2-styryl-benzoxazole or -naphthoxazoles, benzimidazole-benzofurans and oxanilides;
- the additional coadditive is a metal chelating agent, preferably ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA),

hydroxyethylethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA) or diethylenetriaminepentamethylenephosphonic acid (DTPMPA);

- the additional coadditive is a mixture of a UV absorber and polymeric inhibitor;
- the additional coadditive is a mixture of a UV absorber and a fluorescent whitening agent;
- the additional coadditive is a mixture of a UV absorber and metal chelating agent;
- the additional coadditive is a mixture of a polymeric inhibitor and a fluorescent whitening agent;
- the additional coadditive is a mixture of a polymeric inhibitor and a metal chelating agent;
- the additional coadditive is a mixture of a fluorescent whitening agent and a metal chelating agent;
- the additional coadditive is a mixture of a UV absorber, a polymeric inhibitor and a metal chelating agent;
- the additional coadditive is a mixture of a fluorescent whitening agent, a polymeric inhibitor and a metal chelating agent.

Typical and useful UV absorbers are, for example,

- (a) 5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
- (b) 2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
- (c) 2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole;
- (d) 2-(2-hydroxy-3,5-di- $\alpha$ -cumylphenyl)-2H-benzotriazole;
- (e) 2-(2-hydroxy-3- $\alpha$ -cumyl-5-tert-octylphenyl)-2H-benzotriazole;
- (f) 2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole;
- (g) 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)- benzenesulfonic acid monosodium salt;
- (h) 3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamic acid and sodium salt;
- (i) 12-hydroxy-3,6,9-trioxadodecyl 3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamate;
- (j) octyl 3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamate;
- (k) 4,6-bis(2,4-dimethylphenyl)-2-(4-(3-dodecyloxy\*-2-hydroxypropoxy)-2-hydroxyphenyl)-s-triazine (\*is mixture of C<sub>12-14</sub>Oxy isomers);
- (l) 4,6-bis(2,4-dimethylphenyl)-2-(4-octyloxy-2-hydroxyphenyl)-s-triazine;

- (m) 2,4-dihydroxybenzophenone;
- (n) 2,2'-dihydroxy-4,4'-dimethoxy-5,5'-disulfobenzophenone, disodium salt;
- (o) 2-hydroxy-4-octyloxybenzophenone;
- (p) 2-hydroxy-4-dodecyloxybenzophenone;
- (q) 2,4-dihydroxybenzophenone;
- (r) 2,2',4,4'-tetrahydroxybenzophenone;
- (s) 4-aminobenzoic acid;
- (t) 2,3-dihydroxypropyl-4-aminobenzoic acid;
- (u) 3-(4-imidazolyl)acrylic acid;
- (v) 2-phenyl-5-benzimidazole sulfonic acid;
- (w) N,N,N-trimethyl- $\alpha$ -(2-oxo-3-bornylidene)-p-toluidinium methyl sulfate;
- (x) 5-benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid, sodium salt;
- (y) 3-(4-benzoyl-3-hydroxyphenoxy)-2-hydroxy-N,N,N-trimethyl-1-propanaminium chloride;
- (z) 3-[4-(2H-benzotriazol-2-yl)-3-hydroxyphenoxy]-2-hydroxy-N,N,N-trimethyl-1-propanaminium, chloride;
- (aa) 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole; and
- (bb) 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (Uvinul® 3049).

Preferred UV absorbers are

- (a) 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-benzenesulfonic acid monosodium salt;
- (b) 3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamic acid and sodium salt;
- (c) 2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
- (d) 2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole;
- (e) 4,6-bis(2,4-dimethylphenyl)-2-(4-(3-dodecyloxy\*-2-hydroxypropoxy)-2-hydroxyphenyl)-s-triazine (\*is mixture of C<sub>12-14</sub>oxy isomers);
- (f) 12-hydroxy-3,6,9-trioxadodecyl 3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamate;
- (g) 2,4-dihydroxybenzophenone;
- (h) 2,2'-dihydroxy-4,4'-dimethoxy-5,5'-disulfobenzophenone, disodium salt;

- (i) 2,2',4,4'-tetrahydroxybenzophenone;
- (j) 3-(4-benzoyl-3-hydroxyphenoxy)-2-hydroxy-N,N,N-trimethyl-1-propanaminium chloride;
- (k) 3-[4-(2H-benzotriazol-2-yl)-3-hydroxyphenoxy]-2-hydroxy-N,N,N-trimethyl-1-propanaminium, chloride;
- (l) 5-benzoyl-4-hydroxy-2-methoxy-benzenesulfonic acid, sodium salt
- (m) 2-(2-hydroxy-3- $\alpha$ -cumyl-5-tert-octylphenyl)-2H-benzotriazole.

Other preferred compositions are those which additionally contain a metal chelating agent, i.e. those that offer thermodynamic or kinetic control of metal ions. Examples kinetic controlling chelating agents are citrates, keto acids, gluconates, heptagluconates, phosphates, and phosphonates. Examples of chelating agents that offer thermodynamic control are the aminocarboxylic acid chelates. Well known and commercially available members of this class include ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA) and diethylenetriaminepentamethylenephosphonic acid (DTPMPA).

Still other preferred compositions are those which contain mixtures of thermodynamic and kinetic controlling chelating agents are also preferred.

Still other preferred compositions are those which additionally contain a polymeric inhibitor; preferably poly(ethylene glycol) (PEO), poly(propylene glycol) (PPO), poly(butylene glycol) (PTHF), poly(vinyl pyrrolidone) (PVP) or thiol-capped poly(ethylene glycol) as well as copolymers such as poly(ethylene/propylene glycol).

Still other preferred compositions are those which additional contain a fluorescent whitening agent selected from a wide range of chemical types such as 4,4'-bis-(triazinylamino)-stilbene-2,2'-disulfonic acids, 4,4'-bis-(triazol-2-yl)stilbene-2,2'-disulfonic acids, 4,4'-dibenzofuranyl-biphenyls, 4,4'-(diphenyl)-stilbenes, 4,4'-distyryl-biphenyls, 4-phenyl-4'-benzoxazolyl-stilbenes, stilbenyl-naphthotriazoles, 4-styryl-stilbenes, bis-(benzoxazol-2-yl) derivatives, bis-(benzimidazol-2-yl) derivatives, coumarins, pyrazolines, naphthalimides, triazinyl-pyrenes, 2-styryl-benzoxazole or -naphthoxazoles, benzimidazole-benzofurans or oxanilides.



Some preferred compositions contain a mixture of additional stabilizers such as a mixture of a UV absorber and polymeric inhibitor; or a mixture of a UV absorber and a metal chelating agent; or a mixture of a polymeric inhibitor and a metal chelating agent; or a mixture of a polymeric inhibitor and a fluorescent whitening agent; or a mixture of a fluorescent whitening agent and a metal chelating agent; or a mixture of a UV absorber, metal chelating agent and a polymeric inhibitor; or a mixture of fluorescent whitening agent, metal chelating agent and polymeric inhibitor.

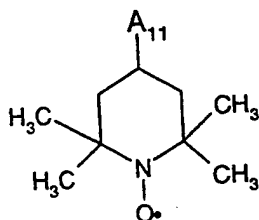
Preferably the compositions are those wherein the compound of formula I or II is of low molecular weight or contains hydrophilic moieties especially cationic groups, is both of low molecular weight and contains hydrophilic moieties.

The instant invention also pertains to a process for preventing the loss of brightness and for enhancing resistance to yellowing of chemimechanical or thermomechanical pulp or paper which still contains lignin, which comprises

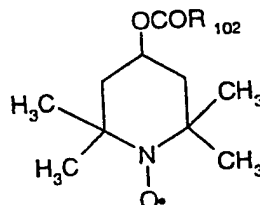
treating said pulp or paper with an effective stabilizing amount of a compound of formula I or II, preferably a compound of formula A to EE or A\* to EE\* as described above.

Preferably the process is that where in the compound of formula A to EE or A\* to EE\*, E is oxyl or hydroxyl and most preferably E is hydroxyl.

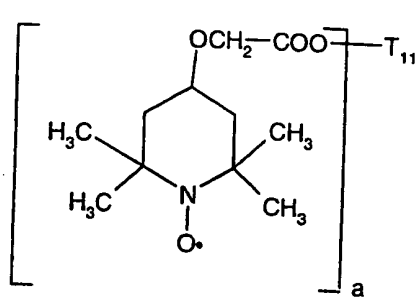
Further compounds useful within this invention are those of formula III, IIIa, IIIb or IIIc



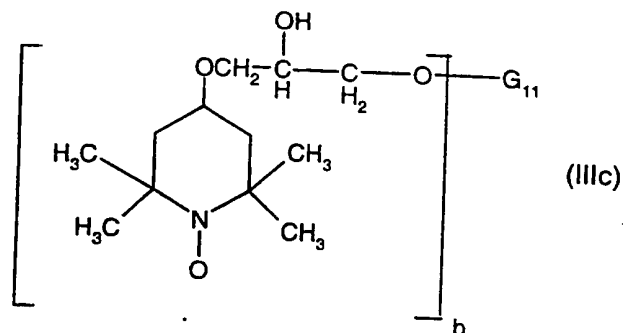
(III),



(IIIa),



(IIIb),



(IIIc)

wherein

$A_{11}$  is  $OR_{101}$  or  $NR_{111}R_{112}$

$R_{101}$  is alkenyl of 2 to 4 carbon atoms, propargyl, glycidyl, alkyl of 2 to 6 carbon atoms interrupted by one or two oxygen atoms, substituted by one to three hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or  $R_{101}$  is alkyl of 1 to 4 carbon atoms substituted by carboxy or by the alkali metal, ammonium or  $C_1$ - $C_4$ alkylammonium salts thereof; or  $R_{101}$  is alkyl substituted by  $-COOE_{10}$  where  $E_{10}$  is methyl or ethyl,

$R_{102}$  is alkyl of 3 to 5 carbon atoms interrupted by  $-COO-$  or by  $-CO$ , or  $R_{102}$  is  $-CH_2(OCH_2CH_2)_cOCH_3$  where  $c$  is 1 to 4; or

$R_{102}$  is  $-NHR_{103}$  where  $R_{103}$  is alkyl of 1 to 4 carbon atoms,

$a$  is 2 to 4,

when  $a$  is 2,  $T_{11}$  is  $-(CH_2CHR_{100}-O)_dCH_2CHR_{100}-$ , where  $d$  is 0 or 1, and  $R_{100}$  is hydrogen or methyl,

when  $a$  is 3,  $T_{11}$  is glyceryl,

when  $a$  is 4,  $T_{11}$  is neopentantetrayl,

$b$  is 2 or 3,

when  $b$  is 2,  $G_{11}$  is  $-(CH_2CHR_{100}-O)_eCH_2CHR_{100}-$ , where  $e$  is 0 to 3, and  $R_{100}$  is hydrogen or methyl, and

when  $b$  is 3,  $G_{11}$  is glyceryl;

$R_{111}$  is hydrogen, alkyl of 1 to 4 carbon atoms, or said alkyl substituted by one or two hydroxyl, interrupted by one or two oxygen atoms, or both substituted by one hydroxyl and interrupted by one or two oxygen atoms,

$R_{112}$  is  $-CO-R_{113}$  where  $R_{113}$  has the same meaning as  $R_{111}$ , or  $R_{112}$  is  $-NHR_{114}$  wherein  $R_{114}$  is alkyl of 1 to 4 carbon atoms, said alkyl substituted by one or two hydroxyl, substituted by alkoxy of 1 to 2 carbon atoms, or said alkyl both substituted by one hydroxyl and by one alkoxy of 1 to

2 carbon atoms, or

$R_{111}$  and  $R_{112}$  together are  $-\text{CO}-\text{CH}_2\text{CH}_2-\text{CO}-$ ,  $-\text{CO}-\text{CH}=\text{CH}-\text{CO}-$  or  $-(\text{CH}_2)_6-\text{CO}-$ ; and with the proviso that, when  $R_{113}$  is alkyl of 1 to 4 carbon atoms,  $R_{111}$  is not hydrogen.

Preferably in the compound of formula III,  $R_{101}$  is allyl, methallyl, glycidyl, 2,3-dihydroxypropyl, 2-hydroxy-4-oxapentyl or  $-\text{CH}_2\text{COOH}$ .

Preferably in the compound of formula IIIa,  $R_{102}$  is methoxymethyl, 2-methoxyethoxymethyl, 2-(2-methoxyethoxy)ethoxymethyl,  $-\text{CH}_2\text{COCH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{COOCH}_3$  or butylamino.

Preferably in the compound of formula IIIb, a is 2,  $T_{11}$  is  $-(\text{CH}_2\text{CHR}-\text{O})_d\text{CH}_2\text{CHR}_{100}-$ , where d is 0, and  $R_{100}$  is hydrogen.

Preferably in the compound of formula IIIc, b is 2,  $G_{11}$  is  $-(\text{CH}_2\text{CHR}-\text{O})_e\text{CH}_2\text{CHR}_{100}-$ , where e is 0 or 1, and  $R_{100}$  is hydrogen.

Preferably in the compound of formula III,  $R_{111}$  is hydrogen or n-butyl.

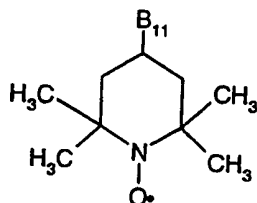
Preferably in the compound of formula III,  $R_{112}$  is  $-\text{CO}-R_{113}$  where  $R_{113}$  is hydrogen, methyl, ethyl, n-propyl, isopropyl, methoxymethyl or 2-methoxyethoxymethyl; or  $R_{102}$  is N-butyl-carbamoyl.

Preferred compounds of formula III or formula IIIa are:

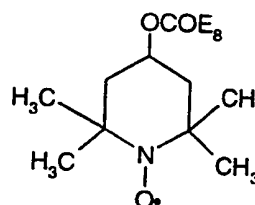
- (a) 1-oxyl-2,2,6,6-tetramethyl-4-allyloxypiperidine;
- (b) 1-oxyl-2,2,6,6-tetramethyl-4-(2-methoxyethoxy)piperidine;
- (c) 1-oxyl-2,2,6,6-tetramethyl-4-glycidioxypiperidine;
- (d) 1-oxyl-2,2,6,6-tetramethyl-4-(2,3-dihydroxypropoxy)piperidine;
- (e) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine;
- (f) 1-oxyl-2,2,6,6-tetramethyl-4-(carboethoxymethoxy)piperidine;
- (g) 1-oxyl-2,2,6,6-tetramethyl-4-(carboxymethoxy)piperidine;
- (h) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-methoxyethoxyacetate;
- (i) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-(2-methoxyethoxy)ethoxyacetate;
- (j) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methoxyacetate;
- (k) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methyl succinate;

- (l) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetoacetate;  
 (m) 1-oxyl-2,2,6,6-tetramethyl-piperidin-4-yl butylcarbamate; or  
 (n) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide,  
 (o) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)methoxyacetamide,  
 (p) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-2-methoxyethoxyacetamide,  
 (q) 1-butyl-3-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)urea,  
 (r) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide,  
 (s) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)acetamide,  
 (t) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)succinimide,  
 (u) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)maleimide, or  
 (v) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)caprolactam. Most preferred among these compounds are (a), (c), (d), (e), (f), (h), (i), (k), (m), (n), (o), (r) and (s); especially preferred are (a), (d), (e) and (r).

Also preferred are compounds of formulae IIIId and IIIe:



(IIIId),



(IIIIe),

wherein

$B_{11}$  is  $OE_9$  or  $NE_{11}E_{12}$

$E_9$  is alkyl of 2 to 6 carbon atoms interrupted by one or two oxygen atoms, substituted by two to three hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or  $E_9$  is alkyl of 1 to 4 carbon atoms substituted by carboxy or by the alkali metal, ammonium or lower alkylammonium salts thereof; or  $E_9$  is alkyl substituted by  $-COOE_{10}$  where  $E_{10}$  is methyl or ethyl, and

$E_8$  is alkyl of 3 to 5 carbon atoms interrupted by  $-COO-$  or by  $-CO-$ , or  $E_8$  is  $-CH_2(OCH_2CH_2)_aOCH_3$  where  $a$  is 1 to 4; or

$E_8$  is  $-NHE_7$  where  $E_7$  is alkyl of 1 to 4 carbon atoms;

$E_{11}$  is hydrogen or alkyl of 1 to 4 carbon atoms, and

$E_{12}$  is  $-CO-E_{13}$  where  $E_{13}$  is alkyl of 1 to 4 carbon atoms which alkyl is interrupted by one or two oxygen atoms, or  $E_{13}$  is  $-NHE_{14}$  where  $E_{14}$  is alkyl of 1 to 4 carbon atoms;

with the proviso that E<sub>9</sub> is not 2,3-dihydroxypropyl.

Preferred compounds are those wherein E<sub>9</sub> is 2-hydroxy-4-oxapentyl or -CH<sub>2</sub>COOH  
Other preferred compounds are those where E<sub>11</sub> is hydrogen or butyl, E<sub>13</sub> is methoxymethyl or 2-methoxyethoxymethyl; or E<sub>12</sub> is N-butylcarbamoyl.

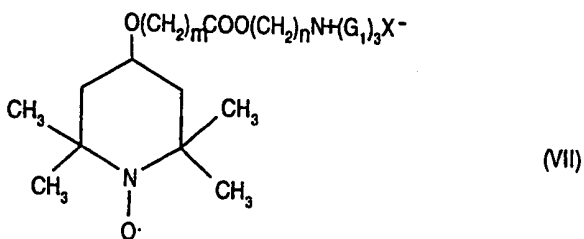
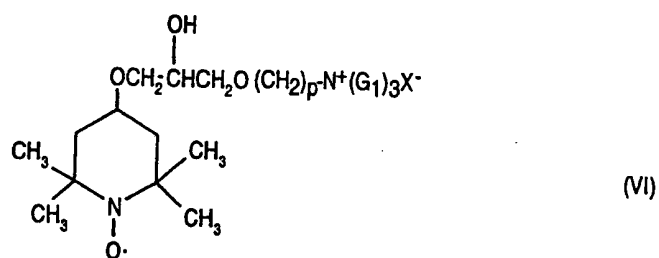
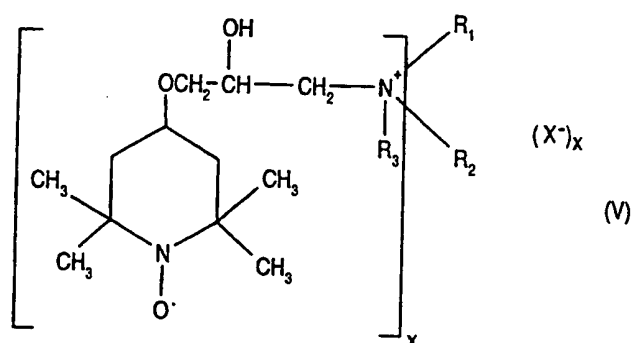
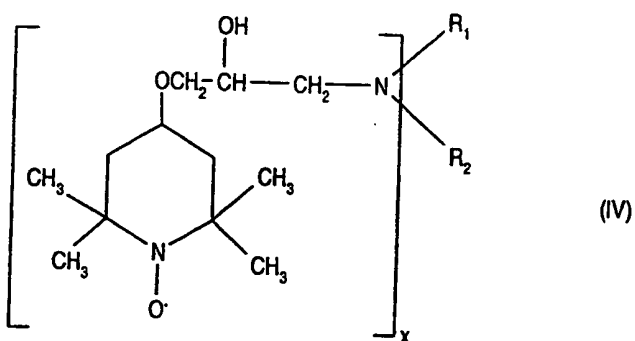
Also preferred compounds are those wherein E<sub>8</sub> is methoxymethyl, 2-methoxyethoxymethyl, 2-(2-methoxyethoxy)ethoxymethyl, -CH<sub>2</sub>COCH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub> or butylamino.

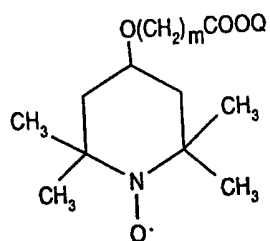
Specifically preferred compounds are:

1-oxy-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxyl)piperidine,  
1-oxy-2,2,6,6-tetramethyl-4-(carboxymethoxyl)piperidine,  
1-oxy-2,2,6,6-tetramethylpiperidin-4-yl 2-(2-methoxyethoxy)ethoxyacetate,  
1-oxy-2,2,6,6-tetramethylpiperidin-4-yl methoxyacetate,  
1-oxy-2,2,6,6-tetramethylpiperidin-4-yl methyl succinate,  
N-(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)methoxyacetamide,  
N-(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)-2-methoxyethoxyacetamide, or  
1-butyl-3-(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)urea.

The compounds of formula III, IIIa, IIIb, IIIc, IIId and IIIE can be prepared with standard methods of organic chemistry according to methods known in the art or in analogy to those methods. The intermediates are partially commercially available.

The instant invention also pertains to new compounds of formula IV, V, VI, VII or VIII





(VIII)

wherein

n is 2 to 3,

G<sub>1</sub> is hydrogen, methyl, ethyl, butyl or benzyl,

X is an inorganic or organic anion, such as described above for some compounds of component (b) of the instant compositions,

m is 1 to 4,

x is 1 to 4,

when x is 1, R<sub>1</sub> and R<sub>2</sub> are independently alkyl of 1 to 18 carbon atoms, said alkyl interrupted by one to five oxygen atoms, said alkyl substituted by 1 to 5 hydroxyl groups or said alkyl both interrupted by said oxygen atoms and substituted by said hydroxyl groups; cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one to three alkyl of 1 to 8 carbon atoms, or R<sub>1</sub> is also hydrogen,

or R<sub>1</sub> and R<sub>2</sub> are together tetramethylene, pentamethylene, hexamethylene or 3-oxapentamethylene,

when x is 2,

$R_1$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or said alkyl both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

$R_2$  is alkylene of 2 to 18 carbon atoms, said alkylene interrupted by one to five oxygen atoms, said alkylene substituted by 1 to 5 hydroxyl groups or said alkylene both interrupted by said oxygen atoms and substituted by said hydroxyl groups; o-, m- or p-phenylene or said phenylene substituted by one or two alkyl of 1 to 4 carbon atoms, or

$R_2$  is  $-(CH_2)_kO[(CH_2)_kO]_h(CH_2)_k-$  where  $k$  is 2 to 4 and  $h$  is 1 to 40, or

$R_1$  and  $R_2$  together with the two N atoms to which they are attached are piperazin-1,4-diyl,

when  $x$  is 3,

$R_1$  is hydrogen,

$R_2$  is alkylene of 4 to 8 carbon atoms interrupted by one nitrogen atom,

when  $x$  is 4,

$R_1$  is hydrogen,

$R_2$  is alkylene of 6 to 12 carbon atoms interrupted by two nitrogen atoms,

$R_3$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

$p$  is 2 or 3, and

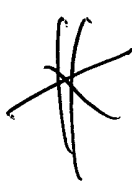
$Q$  is an alkali metal salt, ammonium or  $N^+(G_1)_4$ .



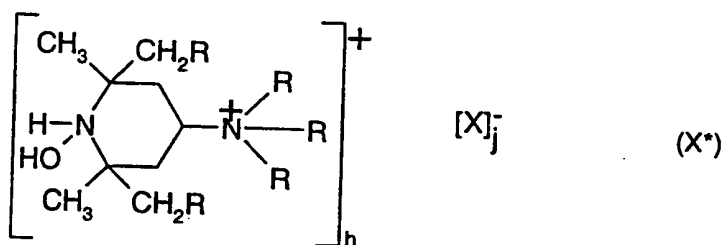
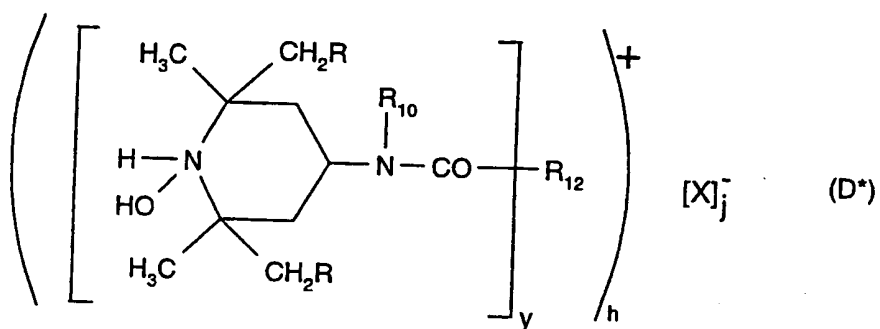
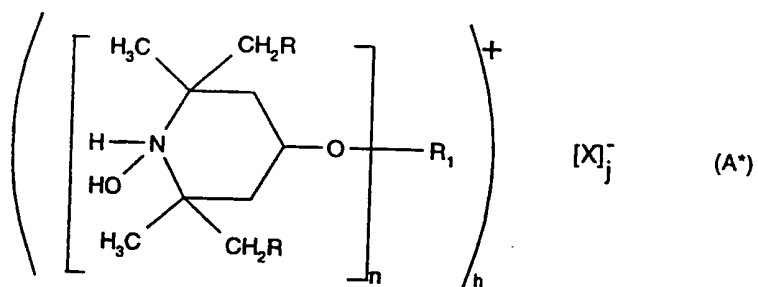
Preferably, in the compounds of formulas IV to VIII

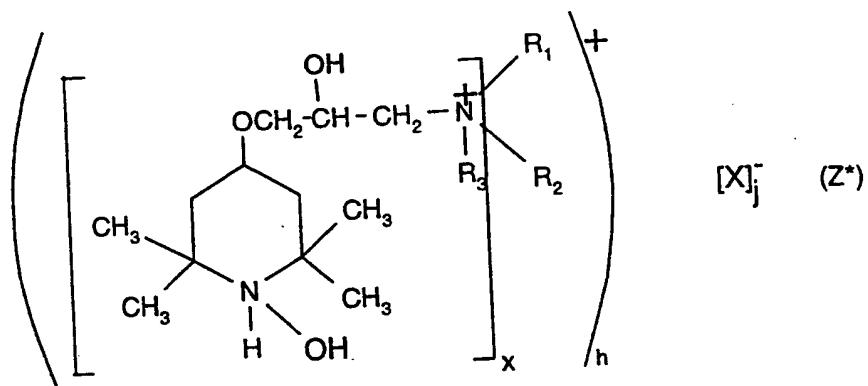
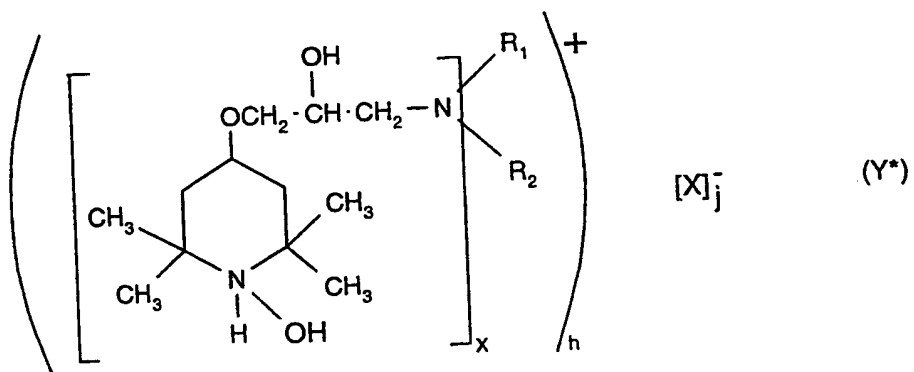
n is 2; G<sub>1</sub> is hydrogen or methyl; X is chloro or bromo; x is 1 or 2, R<sub>1</sub> and R<sub>2</sub> are independently alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or said alkyl both interrupted by one or two oxygen atoms and substituted by a hydroxyl group, or R<sub>1</sub> is hydrogen; or R<sub>1</sub> and R<sub>2</sub> together are 3-oxapentamethylene; R<sub>3</sub> is hydrogen or alkyl of 1 to 2 carbon atoms, or said alkyl substituted by a hydroxyl group, p is 2, m is 1, and Q is Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup> or N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup>.

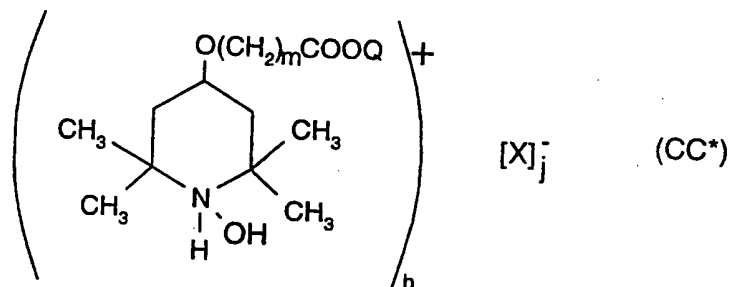
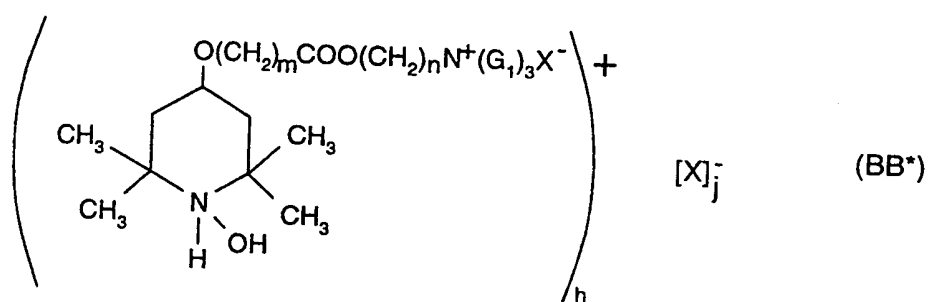
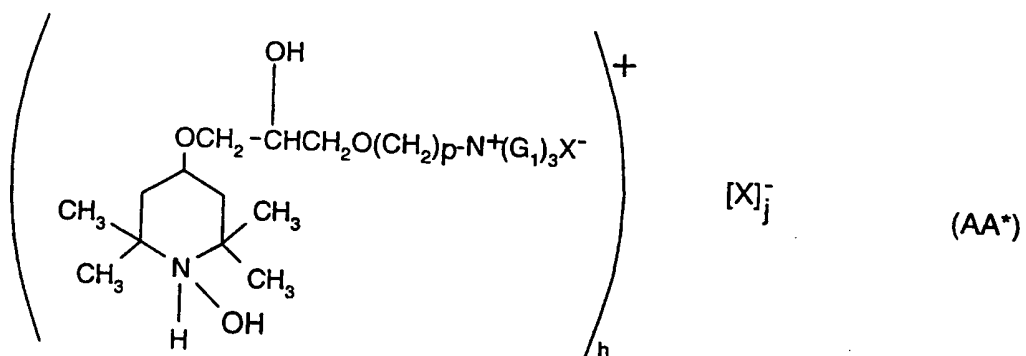
Typical compounds falling within the structures of formulas IV to VIII and which are useful in this invention are:

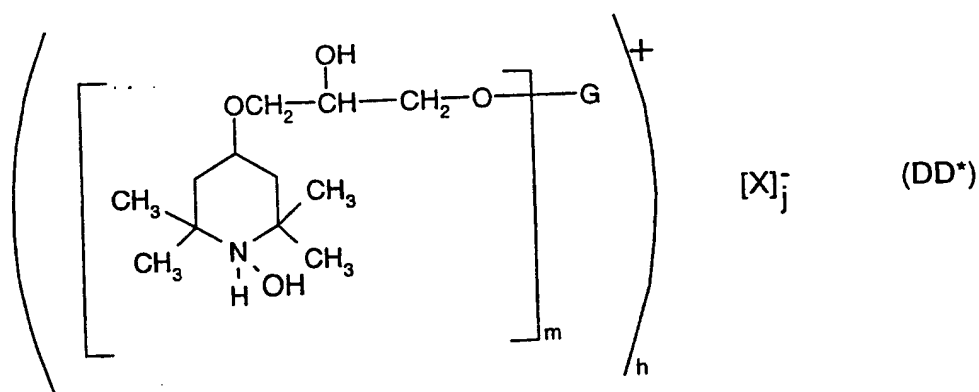
- 
- (a) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxa-6-trimethylammoniumhexyloxy) piperidine chloride;
  - (b) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-3-trimethylammoniumpropoxy) piperidine chloride;
  - (c) 1-oxyl-2,2,6,6-tetramethyl-4-{2-hydroxy-3-[di(2-hydroxyethyl)amino]propoxy} piperidine;
  - (d) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-3-dimethylaminopropoxy) piperidine;
  - (e) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-3-diethylaminopropoxy) piperidine;
  - (f) N,N'-dimethyl-N,N'-bis-[3-(1-oxyl-2,2,6,6-tetramethyl-piperidin-4-yloxy)-2-hydroxypropyl]hexamethylenediamine;
  - (g) N,N,N',N'-tetramethyl-N,N'-bis-[3-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yloxy)-2-hydroxypropyl]-hexamethylenediammonium dibromide;
  - (h) 1-oxyl-2,2,6,6-tetramethyl-4-[2-hydroxy-3-(N,N-dimethyl-N-propylammonium)propoxy] piperidine chloride;
  - (i) sodium 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yloxyacetate; or
  - (j) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yloxyacetic acid, choline ester.

The instant invention also pertains to novel hydroxylamine salts of formulae A\*, D\*, X\*, Y\*, Z\*, AA\*, BB\*, CC\* and DD\*.









R is hydrogen,

in formula A\*  
wherein

n is 1,

R<sub>1</sub> is hydrogen or alkyl of 1 to 4 carbon atoms, preferably hydrogen,

in formula D\*

y is 1,

R<sub>10</sub> is hydrogen or methyl, preferably hydrogen,

R<sub>12</sub> is alkyl of 1 to 4 carbon atoms, preferably methyl,

X is phosphate, phosphonate, carbonate, bicarbonate, nitrate, chloride, bromide, bisulfite, sulfite, bisulfate, sulfate, borate, formate, acetate, benzoate, citrate, oxalate, tartrate, acrylate, polyacrylate, fumarate, maleate, itaconate, glycolate, gluconate, malate, mandelate, tiglate, ascorbate, polymethacrylate, a carboxylate of nitrilotriacetic acid, hydroxyethylethylenediamine-triacetic acid, ethylenediaminetetraacetic acid or of diethylenetriaminepentaacetic acid, a diethylenetriaminepentamethylenephosphonate, an alkylsulfonate or an arylsulfonate,

where the total charge of cations  $h$  is equal to the total charge of anions  $j$ ,

wherein in formulas  $X^*$  to  $DD^*$

$n$  is 2 to 3,

$G_1$  is hydrogen, methyl, ethyl, butyl or benzyl,

$m$  is 1 to 4,

$x$  is 1 to 4,

when  $x$  is 1,  $R_1$  and  $R_2$  are independently alkyl of 1 to 18 carbon atoms, said alkyl interrupted by one to five oxygen atoms, said alkyl substituted by 1 to 5 hydroxyl groups or said alkyl both interrupted by said oxygen atoms and substituted by said hydroxyl groups; cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one to three alkyl of 1 to 8 carbon atoms, or  $R_1$  is also hydrogen,

or  $R_1$  and  $R_2$  are together tetramethylene, pentamethylene, hexamethylene or 3-oxapentamethylene,

when  $x$  is 2,

$R_1$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or said alkyl both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

$R_2$  is alkylene of 2 to 18 carbon atoms, said alkylene interrupted by one to five oxygen atoms, said alkylene substituted by 1 to 5 hydroxyl groups or said alkylene both interrupted by said oxygen atoms and substituted by said hydroxyl groups; o-, m- or p-phenylene or said phenylene substituted by one or two alkyl of 1 to 4 carbon atoms, or

$R_2$  is  $-(CH_2)_kO[(CH_2)_kO]_h(CH_2)_k-$  where  $k$  is 2 to 4 and  $h$  is 1 to 40, or

$R_1$  and  $R_2$  together with the two N atoms to which they are attached are piperazin-1,4-diyl,

when  $x$  is 3,

$R_1$  is hydrogen,

$R_2$  is alkylene of 4 to 8 carbon atoms interrupted by one nitrogen atom,

when  $x$  is 4,

$R_1$  is hydrogen,

$R_2$  is alkylene of 6 to 12 carbon atoms interrupted by two nitrogen atoms,

$R_3$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

$p$  is 2 or 3, and

$Q$  is an alkali metal salt, ammonium or  $N^+(G_1)_4$ ,

in formula DD and DD\*

$m$  is 2 or 3,

when  $m$  is 2,  $G$  is  $-(CH_2CHR-O)_rCH_2CHR-$ , where  $r$  is 0 to 3, and  $R$  is hydrogen or methyl,

and

when m is 3, G is glyceryl,

with the proviso that in formula A\* when R<sub>1</sub> is hydrogen, X is not chloride or bisulfate, and when in formula D\* when R<sub>10</sub> is hydrogen and R<sub>12</sub> is methyl, X is not chloride or bisulfate.

Preferred anions X for the novel compounds and hydroxylammonium salts of this invention are as defined above for the compounds of component (b) of compositions of the invention. For example, X is preferably chloride, bisulfate, bisulfite, sulfate, nitrate, acetate, citrate or carboxylate of ethylenediaminetetraacetic acid or diethylenetriaminepentaacetic acid; most preferably, X is bisulfate or citrate.

Hydroxylamine salts of particular interest are:



- (a) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium citrate;
- (b) bis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) citrate;
- (c) tris(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) citrate;
- (d) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium DTPA;
- (e) bis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) DTPA;
- (f) tris(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) DTPA;
- (g) tetrakis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) DTPA;
- (h) pentakis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) DTPA;
- (i) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium EDTA;
- (j) bis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) EDTA;
- (k) tris(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) EDTA;
- (l) tetrakis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) EDTA;
- (m) 1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium citrate;
- (n) bis(1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium) citrate;
- (o) tris(1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium) citrate;
- (p) 1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium DTPA;
- (q) bis(1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium) DTPA;
- (r) tris(1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium) DTPA;
- (s) tetrakis(1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium) DTPA;
- (t) pentakis(1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium) DTPA;
- (u) 1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium EDTA;
- (v) bis(1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium) EDTA;
- (w) tris(1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium) EDTA;
- (x) tetrakis(1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium) EDTA;
- (y) 1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium citrate;
- (z) bis(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) citrate;
- (aa) tris(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) citrate;
- (bb) 1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium DTPA;
- (cc) bis(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) DTPA;

- (dd) tris(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) DTPA;
- (ee) tetrakis(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) DTPA;
- (ff) pentakis(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) DTPA;
- (gg) 1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium EDTA;
- (hh) bis(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) EDTA;
- (ii) tris(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) EDTA;
- (jj) tetrakis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) EDTA;
- (kk) 1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium citrate;
- (ll) bis(1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium) citrate;
- (mm) tris(1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium) citrate;
- (nn) 1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium DTPA;
- (oo) bis(1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium) DTPA;
- (pp) tris(1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium) DTPA;
- (qq) tetrakis(1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium) DTPA;
- (rr) pentakis(1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium) DTPA;
- (ss) 1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium EDTA;
- (tt) bis(1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium) EDTA;
- (uu) tris(1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium) EDTA or
- (vv) tetrakis(1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium) EDTA.

Nitroxides, hydroxylamines and their salts alone or in combination with UV absorbers are also effective in improving the resistance to yellowing of mechanical pulps which have been modified by acylation, alkylation, treatment with sodium borohydride or hydrogenated.

The intermediates needed to make the instant compounds are largely items of commerce.

The effective stabilizing amounts of the hindered amine is 0.001 to 5 % by weight based on the pulp or paper. Preferably, the effective stabilizing amount is 0.005 to 2 % by weight; preferably 0.01 to 1% by weight.

When a coadditive stabilizer is also present, the effective stabilizing amount of the coadditives is also 0.001 to 5 % by weight based on the pulp or paper; preferably 0.005 to 2 % by weight; most preferably 0.01 to 2% by weight.

The instant inhibitor additive system can be added to pulp or paper at a number of places during the manufacturing or processing operations. These include

- a. on a pulp slurry in the latency chest;
- b. on a pulp slurry in or after the bleaching stage in a storage, blending or transfer chest;
- c. on pulp during or after bleaching, washing and dewatering followed by cylinder or flash drying;
- d. before or after the cleaners;
- e. before or after the fan pump to the paper machine headbox;
- f. to the paper machine white water;
- g. to the silo or save all;
- h. in the press section using a size press, coater or spray bar;
- i. in the drying section using a size press, coater or spray bar;
- j. on the calender using a wafer box; and/or
- k. on paper in an off-machine coater or size press; and/or
- l. in the curl control unit.

Clearly, the precise location where the stabilizer additives should be added will depend on the specific equipment involved, the exact process conditions being used and the like. In some cases, the additives may be added at one or more locations for most effectiveness.

At these various locations, the instant inhibitor additive system can also be added with a carrier or additive typically used in paper making, such as retention aids, sizing aids and solutions, starches, precipitated calcium carbonate, ground calcium carbonate, or other clays or fillers, and brightening additives.

The following examples are for illustrative purposes only and are not to be construed to limit the instant invention in any manner whatsoever.

### Handsheet Treatment

All additives are applied by syringe-injecting the appropriate weight % of additive combination in either an aqueous solution when the additive is water soluble, or a solution in 1:1 (ethanol/dioxane) onto bleached thermomechanical pulp (BTMP) brightness squares (4 cm x 4cm). The clamped sheets are allowed to air dry for one day.

The brightness of the handsheets is recorded before and after treatment by light exposure.

Accelerated testing is carried out by subjecting the treated sheets to accelerated light induced yellowing in a fan-cooled light box containing eight fluorescent lamps with a spectral maximum output at 5700 Å with a total output approximately 43 times greater than normal office fluorescent lamps. The lamps are only about ten inches away from the handsheets being illuminated.

Ambient testing is carried out by placing the treated handsheets on a desk under normal cool-white fluorescent office lights at a nominal distance of six feet.

In both case ISO brightness is tracked as a function of photolysis time and converted to post color number (PC number) in the usual manner. (Giertz, Svensk Papperstidn, (1945) 48 (13), 317)

Post color (PC) number is defined as follows:

$$PC = [(k/s)_{\text{after}} - (k/s)_{\text{before}}] \times 100$$

$$k/s = (1 - R_{\text{inf}})^2 / 2 R_{\text{inf}}$$

where k and s are the absorption and scattering coefficients, respectively, and  $R_{\text{inf}}$  is the value of ISO brightness.

The relationship between  $R_{int}$  and the chromophore concentration is non-linear, whereas, the PC number is roughly linearly related to the concentration of the chromophore in the sample.

Low PC numbers are desired as they indicate less yellowing.

When using the ambient test conditions untreated BTMP handsheets are compared to Kraft handsheets, after 60 days the BTMP handsheets have a PC number which is about 10 while the Kraft paper has a PC number which is 0.388742. The Kraft handsheets are clearly less yellow than untreated BTMP handsheets after exposure to ambient light.

The incident light flux for the accelerated yellowing experiments (Examples 1-4) is 43 times greater than normal office fluorescent lamps as measured by the A. W. Speery SLM-110 digital light power meter. The brightness of the handsheets is tracked and compared to that of untreated sheets exposed in the same manner. The treated sheets exhibit significant resistance to yellowing as seen below.

#### Materials Used in the Examples

Compound A is 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidine;  
Compound B is 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine;  
Compound C is 1-oxyl-2,2,6,6-tetramethyl-4-acetamidopiperidine;  
Compound D is 1-oxyl-2,2,6,6-tetramethylpiperidine TEMPO;  
Compound E is bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;  
Compound F is 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium chloride;  
Compound G is 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium bisulfate;  
Compound H is bis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) sulfate;  
Compound I is 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium acetate;  
Compound J is pentakis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) diethylenetriaminepentaacetic acid;

- Compound K is 3-(4-benzyloxy-2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionic acid methyl ester (PAX-3008);
- Compound L is 3-(4-{4-[1-(2-methoxycarbonyl-ethoxy)-2,2,6,6-tetramethyl-piperidin-4-yloxymethyl]-benzyloxy}-2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionic acid methyl ester (PAX-3036);
- Compound M is 2,2-diethyl-malonic acid bis-(1-butylcarbamoyloxy-2,2,6,6-tetramethyl-piperidin-4-yl) ester (PAX-3123);
- Compound N is acetic acid 4-hydroxy-2,2,6,6-tetramethyl-piperidin-1-yl ester (PAX-3136);
- Compound O is benzoic acid 1-butoxycarbonyloxy-2,2,6,6-tetramethyl-piperidin-4-yl ester (PAX-3267);
- Compound P is 2,2,6,6-tetramethyl-1-(1-phenyl-ethoxy)-piperidin-4-ol (PAX-3156)
- Compound Q is 2,4-dihydroxybenzophenone;
- Compound R is 12-hydroxy-3,6,9-trioxadodecyl-3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamate (Tinuvin® 1130);
- Compound S is, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-benzenesulfonic acid monosodium salt (Cibafast® W);
- Compound T is 1-oxyl-2,2,6,6-tetramethyl-4-(2,3-dihydroxypropoxy)piperidine;
- Compound U is 1-oxyl-2,2,6,6-tetramethyl-4-(carboxymethoxy)piperidine;
- Compound V is 3-oxyl-1,2,2,4,4-pentamethyl-3,4-dihydro-2.H.-imidazol-1-ium methylsulfate;
- Compound W is 3-(3-benzotriazol-2-yl-5-.tert.-butyl-4-hydroxy-phenyl)-propionic acid CG20-0568;
- Compound X is polyethylene glycol of molecular weight 300 (PEO);
- Compound Y is 4,6-bis(2,4-dimethylphenyl)-2-(4-(3-dodecyloxy\*-2-hydroxypropoxy)-2-hydroxyphenyl)-s-triazine (\* is mixture of C<sub>12-14</sub>oxy isomers) (Tinuvin® 400);
- Compound Z is 2,2'-dihydroxy-4,4'-dimethoxy-5,5'-disulfobenzophenone, disodium salt (Uvinul® 3048);
- Compound AA is 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (Uvinul® 3049);
- Compound BB is diethylenetriamine tetraacidic acid (DTPA);
- Compound CC is 5,5-dimethyl-1-pyrroline N- oxide;
- Compound DD is N-tert-butyl- $\alpha$ -phenylnitrone;
- Compound EE is 1-oxyl-2,2,6,6-tetramethyl-4-oxo-piperidine;

Compound FF is tris(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) citrate;  
 Compound GG is dithiothreitol;  
 Compound HH is 1-thioglycerol;  
 Compound II is 2,2'-oxydiethanethiol;  
 Compound JJ is 2,2,6,6-tetramethyl-4-acetamidopiperidine;  
 Compound KK is UVINUL® 3000, 2,4-dihydroxybenzophenone;  
 Compound LL is Brightener 28; 4,4'-bis[4-anilino-6-(bis(2-hydroxyethyl)amino-s-triazin-2-yl)amino-2,2'-stilbenedisulfonic acid, disodium salt;  
 TMHP is 2,2,6,6-tetramethyl-4-hydroxypiperidine.

### Example 1

#### Accelerated Yellowing with High Intensity Lamps

A BTMP sheet is treated with 0.5%-0.1% by weight of Compound A. The sheets treated with Compound A exhibit substantial inhibition to yellowing compared to the untreated control sheet as seen by the PC numbers.

Time in Days	Concentration					
	0.5%	0.4%	0.3%	0.2%	0.1%	Blank
PC Number						
1.0	1.63	1.51	1.56	1.67	2.13	5.51
2.1	3.05	2.94	3.12	3.35	4.2	9.97
3.0	4.17	4.09	4.37	4.76	5.92	13.14
4.0	5.35	5.26	5.56	6.01	6.82	15.85
5.0	6.28	6.35	6.76	7.24	8.97	18.07
6.1	7.43	7.52	7.87	8.54	10.42	20.4
7.0	8.46	8.66	9.10	9.88	12.09	23.63

Even levels as low as 0.1% by weight of Compound A show effective stabilization effects.

Example 2

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.50% by weight of various hydroxylamine compounds by the procedure of Example 1.

1-hydroxy-2,2,6,6-tetramethyl-1,2,3,6-tetrahydro-pyridine;  
1-hydroxy-2,2,6,6-tetramethyl-4-methoxypiperidine;  
1-hydroxy-2,2,6,6-tetramethyl-4-ethoxypiperidine;  
1-hydroxy-2,2,6,6-tetramethyl-4-propoxypiperidine;  
1-hydroxy-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxypiperidine;  
4,4'-[1,6-hexanediylbis(formylimino)]bis[2,2,6,6-tetramethyl-1-hydroxypiperidine;  
2-(8-carboxy-octyl)-4,4-dimethyl-2-octyl-3-hydroxy-oxazolidine;  
3,3-dimethyl-4-hydroxy-1-oxa-4-azaspiro[4.5]decane;  
3-aminomethyl-2,2,5,5-tetramethyl-1-hydroxy-pyrrolidine;  
3-carboxy-2,2,5,5-tetramethyl-1-hydroxypyrrolidine;  
4-phenyl-2,2,5,5-tetramethyl-1-hydroxy-3-imidazoline;  
4-phenyl-2,2,5,5-tetramethyl-1-hydroxy-3-imidazoline-3-oxide;  
di-tert-butyl hydroxylamine.

The sheets treated with hydroxylamines exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Example 3

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, C, D and E. The sheets treated with nitroxides exhibit substantial inhibition to yellowing compared to the untreated control sheet.



Time in Days	Compounds				
	Blank	B	C	D	E
	PC Number				
0	0	0	0	0	0
0.93	2.49	0.88	1.6	2.01	1.28
1.9	5.27	1.89	3.24	4.06	2.49
2.94	8.46	3.41	5.52	6.73	4.28
3.93	10.54	4.36	6.89	8.57	5.4
4.98	12.34	5.36	8.31	10.5	6.53
5.88	13.81	6.11	9.45	11.62	7.74
6.91	15.55	7.17	11.05	13.17	8.81
7.98	17.34	8.18	12.5	14.57	10.12
8.97	19.44	9.33	13.72	16.28	11.32
10.01	20.98	10.1	15.07	17.75	12.21
10.94	22.35	11.01	16.3	19.1	13.16

Example 4

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound EE. The sheets treated with nitroxides exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in Days	Compound EE	Blank
	PC Number	
	0	0
0		4.53
1.04	1.77	7.91
2.02	3.77	11.16
3.06	5.97	13.72
4.02	7.76	15.47
5.02	9.28	17.61
6.23	10.49	18.78
6.98	11.88	20.09
7.98	13.06	25.25
10.96	16.92	

Example 5

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of each of the following compounds:

- 1-oxyl-2,2,6,6-tetramethyl-1,2,3,6-tetrahydro-pyridine;
- 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl-acetate;
- 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl-2-ethylhexanoate;
- 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl-stearate;
- 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl-benzoate;
- 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl-(4-tert-butyl)benzoate;
- bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-succinate;
- bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-adipate;
- bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-n-butylmalonate;
- bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-phthalate;
- bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-isophthalate;
- bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-terephthalate;
- bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-hexahydroterephthalate;
- N,N'-bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-adipinamide;
- N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-caprolactam;
- N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-dodecylsuccinimide;
- 2,4,6-tris-[N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-s-triazine];
- 4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperazin-3-one);
- tris-(2,2,6,6-tetramethyl-1-oxyl-piperidin-4-yl)phosphite;
- 1-oxyl-2,2,6,6-tetramethyl-4-methoxypiperidine;
- 1-oxyl-2,2,6,6-tetramethyl-4-ethoxypiperidine;
- 1-oxyl-2,2,6,6-tetramethyl-4-propoxypiperidine;
- 1-oxyl-2,2,6,6-tetramethyl-4-carboxypiperidine;
- 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine;
- 4,4'-[1,6-hexanediylbis(formylimino)]bis[2,2,6,6-tetramethyl-1-piperdinyloxy];
- 2-(8-carboxyooctyl)-4,4-dimethyl-2-octyl-3-oxazolidinyloxy;
- 3,3-dimethyl-1-oxa-4-azaspiro[4.5]dec-4-yloxy;
- 3-aminomethyl-2,2,5,5-tetramethyl-1-pyrrolidinyloxy;

3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy;  
 4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy;  
 4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxide;  
 di-tert-butyl nitroxide.

The sheets treated with nitroxides exhibit substantial inhibition to yellowing compared to the untreated control sheet.

### Example 6

#### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.50% by weight of Compounds A, F, G, H, I and J. The sheets treated with hydroxylamine salts exhibit substantial inhibition to yellowing compared to the untreated control sheet.

the untreated control sheet.

		Compounds					
Time in Days	Blank	A	F	G	H	I	J
PC Numbers							
0	0	0	0	0	0	0	0
0.77	3.62	0.90	1.26	1.42	1.23	1.02	1.08
1.74	6.27	1.69	2.29	2.60	2.08	1.97	1.98
2.81	8.82	2.50	3.23	3.54	2.92	2.8	2.84
3.8	10.97	3.25	4.20	5.0	3.85	3.65	3.66
4.75	12.86	4.08	5.01	5.52	4.60	4.3	4.44
5.81	14.68	4.88	5.95	6.6	5.5	5.08	5.36
6.79	16.24	5.62	6.81	7.51	6.27	5.85	6.0
7.8	17.36	6.09	7.40	8.42	6.97	6.36	6.56
8.76	18.44	6.71	8.13	9.24	7.7	7.02	7.13
9.75	19.41	7.33	8.76	9.95	8.3	7.62	7.72
10.8	20.35	7.85	9.43	10.68	8.92	8.26	8.2
11.87	21.13	8.34	9.98	11.36	9.46	8.68	8.6
12.81	21.98	8.77	10.52	12.12	9.98	9.10	9.06

Example 7

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.50% by weight of Compounds K and L. The sheets treated with hindered amine hydroxylamine Compounds K and L exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in Days	Blank	Compounds	
		K	L
PC Number			
0	0	0	0
.81	3.19	1.42	1.59
1.82	5.85	2.62	3.02
2.8	8.06	3.93	4.41
3.75	10.02	4.79	5.42
4.83	12.08	5.85	6.61
5.8	13.81	7.35	7.52
6.76	15.49	7.73	8.40
7.77	16.98	8.39	9.2
8.74	18.54	9.34	10.36
9.76	20.06	10.02	11.18
10.74	21.56	11.06	12.24

Example 8

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.50% by weight of Compounds M, N and O. The sheets treated with selected acylated hindered amine hydroxylamine derivatives exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in Days	Compounds			
	Blank	M	N	O
		PC Number		
0	0	0	0	0
.82	3.87	2.06	2.02	2.05
2.72	8.9	5.28	4.87	5.13
3.76	10.88	6.53	6.03	6.42
4.76	15.59	7.72	7.17	7.62
5.76	14.32	8.92	8.28	8.77
6.77	16.36	10.42	9.61	10.24
7.81	18.47	11.97	10.94	11.7
8.79	20.15	13.14	12.01	12.86
10	21.9	14.31	13.08	13.96
10.77	23.5	15.51	14.02	15.16

Example 9

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.5% by weight of each of the following:

1-acetyl-4-hydroxy-2,2,6,6-tetramethyl-piperidine;

1-acetyl-2,2,6,6-tetramethyl-piperidin-4-one;

bis(1-acetyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

The sheets treated with acylated hindered amine derivatives exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Example 10

Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.50% by weight of Compound P. The sheets treated with Compound P exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in Days	Blank PC Number	Compound P
0	0	0
.81	3.19	1.66
1.82	5.85	2.68
2.8	8.06	3.76
3.75	10.02	4.64
4.83	12.08	5.50
5.8	13.81	6.28
6.76	15.49	7.21
7.77	16.98	7.90
8.74	18.54	8.9
9.76	20.06	9.63
10.74	21.56	10.47

Example 11

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.5%-0.1% by weight of Compound A and 0.5% by weight of Compound Q. The sheets treated with a combination of hydroxylamine and benzophenone UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in Days	Concentration of Compound A					Blank
	0.50	0.40	0.30	0.20	0.10	
	PC Number					
0	0	0	0	0	0	0
1	1.05	0.73	0.71	0.93	0.86	5.74
2.1	2.17	1.63	1.6	2.11	2.02	10.51
2.98	3.05	2.48	2.43	3.12	3.09	13.75
3.98	4.12	3.41	3.39	4.37	4.2	16.67
4.97	4.95	4.22	4.16	5.39	5.15	18.96
6.05	5.95	5.18	5.18	6.59	6.36	21.42

Example 12

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound A and 0.5% by weight of the UVA compounds R and S. The sheets treated with a combination of hydroxylamine and benzotriazole UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of hydroxylamine and UVA are used.

Time in Days	Compound			Blank
	0.25% A	0.25% A 0.5% R	0.25% A 0.5% S	
PC Number				
0	0	0	0	0
0.77	0.97	0.21	0.21	3.74
1.85	1.86	0.48	0.54	7.25
2.78	2.85	0.8	0.83	10.43
5.84	6.42	2.23	2.38	19.5
6.93	7.85	2.93	3.05	21.69
8	8.82	3.32	3.38	23.25

Example 13

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, T, U and V and 0.5% by weight of the UVA compound S. The sheets treated with a combination of nitroxide and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and UVA are used.

Time in Days	0.25% B 0.5% S	0.25% T 0.5% S	0.25% U 0.5% S	0.25% V 0.5% S	0.5% S	Blank
PC Number						
0	0	0	0	0	0	0
0.9	0.54	1.02	1.01	0.29	3.37	4.24
1.9	1.12	2.06	2	2.12	6.49	7.81
2.9	1.86	3.19	3.11	4.17	9.38	10.91
3.96	2.5	4.52	4.29	6.44	12.31	14.04
7.16	5.03	8.63	8.41	12.92	19.98	22.31
7.89	5.6	9.58	9.44	14.43	21.54	24.13



Example 14

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, T, U and V and 0.5% by weight of the benzophenone UVA compounds:

(2-hydroxy-4-octyloxy-phenyl)-phenyl-methanone;  
(2-hydroxy-4-methoxy-phenyl)-phenyl-methanone;  
(4-dodecyloxy-2-hydroxy-phenyl)-phenyl-methanone;  
(2-hydroxy-4-methoxy-phenyl)-(2-hydroxy-phenyl)-methanone;  
bis-(2-hydroxy-4-methoxy-phenyl)-methanone;  
bis-(2,4-dihydroxy-phenyl)-methanone;  
[3-(3-benzoyl-2-hydroxy-6-methoxy-benzyl)-2-hydroxy-4-methoxy-phenyl]-phenyl-methanone;  
2-hydroxy-4-methoxybenzophenone-5-sulfonic acid;  
2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5,5'-disodium sulfonate.

The sheets treated with a combination of nitroxide and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and UVA are used.

Example 15

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, T, U and V and 0.5% by weight of the benzotriazole UVA compounds:

- (a) 5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
- (b) 2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
- (c) 2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole;

- (d) 2-(2-hydroxy-3,5-di- $\alpha$ -cumylphenyl)-2H-benzotriazole;
- (e) 2-(2-hydroxy-3- $\alpha$ -cumyl-5-tert-octylphenyl)-2H-benzotriazole;
- (f) 2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole;
- (g) 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)- benzenesulfonic acid monosodium salt;
- (h) 3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamic acid and sodium salt;
- (i) 12-hydroxy-3,6,9-trioxadodecyl 3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamate;
- (j) octyl 3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamate;
- (k) 4,6-bis(2,4-dimethylphenyl)-2-(4-(3-dodecyloxy\*-2-hydroxypropoxy)-2-hydroxy phenyl)-s-triazine (\*is mixture of C<sub>12-14</sub>oxy isomers);
- (l) 4,6-bis(2,4-dimethylphenyl)-2-(4-octyloxy-2-hydroxyphenyl)-s-triazine;
- (m) 2,4-dihydroxybenzophenone;
- (n) 2,2',4,4'-tetrahydroxy-5,5'-disulfobenzophenone, disodium salt;
- (o) 2-hydroxy-4-octyloxybenzophenone;
- (p) 2-hydroxy-4-dodecyloxybenzophenone;
- (q) 2,4-dihydroxybenzophenone;
- (r) 2,2',4,4'-tetrahydroxybenzophenone;
- (s) 4-aminobenzoic acid;
- (t) 2,3-dihydroxypropyl-4-aminobenzoic acid;
- (u) 3-(4-imidazolyl)acrylic acid;
- (v) 2-phenyl-5-benzimidazole sulfonic acid;
- (w) N,N,N-trimethyl- $\alpha$ -(2-oxo-3-bornylidene)-p-toluidinium methyl sulfate;
- (x) 5-benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid, sodium salt;
- (y) 3-(4-benzoyl-3-hydroxyphenoxy)-2-hydroxy-N,N,N- trimethyl-1-propanaminium chloride;
- (z) 3-[4-(2H- benzotriazol-2-yl)-3-hydroxyphenoxy]- 2-hydroxy-N,N,N-trimethyl-1-propanaminium, chloride;
- (aa) 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole.

The sheets treated with a combination of nitroxide and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and UVA are used.

#### Example 16

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, T, U and V and 0.5% by weight of the triazine UVA compounds:

4,6-bis(2,4-dimethylphenyl)-2-(4-(3-dodecyloxy\*-2-hydroxypropoxy)-2-hydroxyphenyl)-s-triazine (\*mixture of C<sub>12-14</sub>oxy isomers) (Tinuvin 400);

4,6-bis(2,4-dimethylphenyl)-2-(2-hydroxy-4-octyloxyphenyl)-s-triazine;

2,4,6-tris(4-(3-dodecyloxy\*-2-hydroxypropoxy)-2-hydroxyphenyl)-s-triazine (\*mixture of C<sub>12-14</sub>oxy isomers);

2,4-bis(4-(3-dodecyloxy\*-2-hydroxypropoxy)-2-hydroxyphenyl)-6-(2,4-dimethylphenyl)-s-triazine (\*mixture of C<sub>12-14</sub>oxy isomers).

The sheets treated with a combination of nitroxide and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and UVA are used.

#### Example 17

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, T, U and V and 0.5% by weight of the cinnamate UVA compounds:

2-cyano-3,3-diphenyl-2-propenoic acid ethyl ester;  
2-cyano-3,3-diphenyl-2-propenoic acid 2-ethylhexyl ester;  
3-(4-methoxyphenyl)-2-propenoic acid 2-ethylhexyl ester.

The sheets treated with a combination of nitroxide and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and UVA are used

#### Example 18

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, T, U and V and 0.5% by weight of the oxalanilide UVA compounds:

N-(2-ethoxyphenyl)-N'-(4-isododecylphenyl)-ethanediamide;  
N-(2-ethoxyphenyl)-N'-(2-ethylphenyl)-ethanediamide.

The sheets treated with a combination of nitroxide and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and UVA are used.

#### Example 19

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, T, U and V and 0.5% by weight of the salicylate UVA compounds:

2-hydroxy-benzoic acid phenyl ester;

2-hydroxy-benzoic acid 4-(1,1-dimethylethyl)phenyl ester;  
2-hydroxy-benzoic acid 2-ethylhexyl ester;  
2-hydroxy-benzoic acid 4-isopropylbenzyl ester;  
2-hydroxy-benzoic acid 3,3,5-trimethylcyclohexyl ester.

The sheets treated with a combination of nitroxide and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and UVA are used.

#### Example 20

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, T, U and V and 0.5% by weight of the formamidine UVA compounds:

4-[[[(methylphenylamino)methylene]amino]-benzoic acid, ethyl ester;  
4-[[[(ethylphenylamino)methylene]amino]-benzoic acid, ethyl ester.

The sheets treated with a combination of nitroxide and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and UVA are used.

#### Example 21

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, T, U and V and 0.5% by weight of the 4-hydroxybenzoate UVA compounds:

3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzoic acid hexadecyl ester;  
3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzoic acid 2,4-bis(1,1-dimethylethyl)phenyl ester.

The sheets treated with a combination of nitroxide and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and UVA are used.

#### Example 22

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compounds B, T, U and V and 0.5% by weight of the 4-aminobenzoate UVA compounds:

4-aminobenzoic acid;  
2,3-dihydroxypropyl-4-aminobenzoate;  
2-ethylhexyl 4-dimethylaminobenzoate;  
ethyl 4-[bis(2-hydroxypropyl)amino]benzoate.

The sheets treated with a combination of nitroxide and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and UVA are used.

#### Example 23

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.50% by weight of Compounds A, F, G, H, I and J and 0.5% of Compound R. The sheets treated with hydroxylamine salts and UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in Days	0.5% G 0.5% R	0.5% H 0.5% R	0.5% F 0.5% R	0.5% I 0.5% R	0.5% J 0.5% R	0.5% A 0.5% R	Blank
PC Number							
0	0	0	0	0	0	0	0
0.76	0.57	-0.14	0.06	0.16	-0.18	-0.55	3.51
1.85	0.96	0.02	0.32	0.33	0	-0.49	6.43
2.81	1.55	0.17	0.63	0.57	0.25	-0.33	8.77
3.76	1.94	0.38	0.9	0.81	0.48	-0.21	10.89
4.82	2.52	0.57	1.24	1.01	0.66	-0.06	12.99
5.8	2.89	0.68	1.49	1.17	0.87	0.05	14.7
6.82	3.27	0.81	1.64	1.38	1.06	0.14	16.03
7.77	3.84	1.05	2	1.59	1.29	0.3	17.33
8.76	4.05	1.16	2.17	1.75	1.42	0.43	18.22
9.81	4.77	1.38	2.46	1.98	1.67	0.57	19.27
10.88	5.11	1.53	2.69	2.27	1.86	0.69	20.18
11.82	5.51	1.7	2.97	2.45	2.08	0.84	21.03
12.78	5.77	1.89	3.13	2.7	2.25	0.92	22.03

Example 24

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.50% by weight of Compounds K and L and 0.5% by weight of Compound S. The sheets treated with hindered amine hydroxylamine Michael adduct derivatives and a UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in Days	0.5% K 0.5% S	0.5% L 0.5% S PC Number	0.5% S	Blank
0	0	0	0	0
0.81	0	0.04	0.29	3.03
1.82	0.51	0.87	0.89	5.78
2.8	1.08	1.1	1.47	8.11
3.75	1.56	1.65	2.14	10.21
4.83	2.04	2.25	2.83	12.33
5.8	2.64	2.76	3.56	14.13
6.76	2.98	3.23	4.18	15.6
7.77	3.54	3.82	4.93	17.45
8.74	3.97	4.45	5.7	18.98
9.75	4.6	5.18	6.5	30.34
10.74	5.07	5.85	7.39	21.91

Example 25

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.50% by weight of Compounds M, N and O and 0.5% by weight of the UVA Compound W. The sheets treated with selected acylated hindered amine hydroxylamine derivatives and the UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet.



Time in Days	0.5% M 0.5% W	0.5% N 0.5% W	0.5% O 0.5% W	0.5% W	Blank
PC Number					
0	0	0	0	0	0
.82	0.59	0.46	0.51	.79	3.87
2.72	1.84	1.46	1.77	2.25	8.9
3.76	2.43	1.91	2.46	2.90	10.88
4.76	3.09	2.34	3.12	3.52	12.59
5.76	3.84	2.9	3.87	4.32	14.32
6.77	4.75	3.59	4.72	5.12	16.36
7.81	5.7	4.37	5.68	6.09	18.47
8.79	6.55	4.98	6.46	6.86	20.15
10.0	7.43	5.45	7.37	7.7	21.9
10.77	8.28	6.19	8.28	8.64	23.5

Example 26

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.50% by weight of Compound P and 0.5% Compound S. The sheets treated with Compound P in combination with a UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in Days	0.5% P 0.5% S	0.5% S	Blank
	PC Number		
0	0	0	0
0.81	0.06	0.29	3.03
1.82	0.46	0.89	5.78
2.8	0.95	1.47	8.11
3.75	1.37	2.14	10.21
4.83	1.74	2.83	12.33
5.8	2.13	3.56	14.13
6.76	2.5	4.18	15.6
7.77	2.95	4.93	17.45
8.74	3.42	5.7	18.98

#### Example 27

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with and 0.5% Compound S and 0.5% by weight of:

1-acetyl-4-Hydroxy-2,2,6,6-tetramethyl-piperidine;

1-Acetyl-2,2,6,6-tetramethyl-piperidin-4-one;

bis(1-acetyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

The sheets treated with acylated hindered amine derivatives in combination with a UVA exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Example 28

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound A, 0.5% Compound W and 0.5% of Compound X. The sheets treated with hydroxylamine, UVA and PEO exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in Days	0.25% A	0.25% A 0.5% W	0.25% A 0.5% W 0.5% X	Blank
		PC Number		
0	0	0	0	0
0.77	0.97	0.06	0.03	3.74
1.85	1.86	0.28	0.27	7.25
2.78	2.85	0.49	0.46	10.43
5.84	6.42	1.54	1.48	19.5
6.93	7.85	2	1.98	21.69
8	8.82	2.34	2.26	23.25

Example 29

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound A, 0.5% Compound Y, Z and AA and 0.5% of Compound X. The sheets treated with hydroxylamine, UVA and PEO exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in	0.25%	0.25%	0.25%	0.25%	0.25%	0.25%	0.25%	Blank
Days	A	A	A	A	A	A	A	
		0.5% Y	0.5% Y	0.5% Z	0.5% Z	0.5%A	0.5%A	
			0.5% X		0.5% X	A	A	
							0.5% X	

	PC Number							
0	0	0	0	0	0	0	0	0
0.84	1.22	0.34	0.27	1.11	1.09	0.33	0.22	4
1.77	1.94	0.64	0.45	1.32	1.54	0.53	0.43	7.73
4.88	5.48	2.41	1.86	3.87	4.9	2.39	1.67	18.19
5.92	6.9	3.11	2.46	4.82	5.82	3.01	2.09	21.03
6.99	7.64	3.64	2.81	5.34	6.51	3.48	2.41	22.93

### Example 30

#### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.5% by weight of Compound G, 0.25% by weight of Compound W and 0.25% by weight of Compound BB. The sheets treated with hydroxylamine, UVA and metal chelating agent exhibit substantial inhibition to yellowing compared to the untreated control sheet.

Time in Days	0.5% G 0.25% W 0.25% BB	0.5% G 0.25% BB	0.5% G 0.25% W	0.5% G	0.25% BB	Blank
PC Number						
0	0	0	0	0	0	0
0.83	0.13	0.69	0.23	0.76	3.6	3.68
1.79	0.37	1.26	0.48	1.33	6.17	6.19
2.77	0.58	1.82	0.72	1.87	8.41	8.45
3.81	0.84	2.44	1.01	2.46	10.48	10.49
4.9	1.14	3.02	1.35	2.99	12.36	12.19
5.83	1.37	3.53	1.62	3.51	14.05	13.82
6.8	1.62	4.1	1.87	4.07	15.82	15.39
7.77	1.93	4.67	2.23	4.69	17.31	16.59

Example 31

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound B, 0.5% by weight of Compound Q and 1.0% by weight of Compound CC or DD. The results show the effectiveness of nitrones alone, nitrones with a UVA, nitrones with a nitroxide and especially nitrone with a UVA and a nitroxide in inhibition to yellowing compared to the untreated control sheet.

Time in Days	0.5% Q 0.25%B 1 % CC	0.5% Q 0.25% B 1% DD	0.5% Q 1% CC	0.5% Q 1% DD	0.5% Q	0.25% B 1%CC	0.25% B 1% DD	1%CC	1%DD	Blank
PC Number										
0	0	0	0	0	0	0	0	0	0	0
0.74	-1.25	0.13	-0.43	0.25	0.55	-0.43	0.85	0.28	2.14	3.22
1.74	-0.92	0.45	-0.16	0.72	1.19	0.28	2.49	1.82	4.78	7.24
2.82	-0.59	0.84	0.25	1.26	1.82	0.83	3.83	3.69	6.68	9.77
3.83	-0.41	1.33	0.93	1.88	2.63	1.63	5.09	5.88	8.34	12.42
4.76	-0.19	1.75	1.7	2.56	3.53	2.53	6.13	7.8	9.8	14.78
5.75	-0.01	2.08	2.54	3.13	4.41	3.3	6.87	9.63	11.14	16.89
6.77	0.19	2.51	3.35	3.77	5.36	3.96	7.67	11.25	12.33	19.13
7.75	0.44	2.91	4.14	4.36	6.13	4.56	8.23	12.39	13.16	20.09
8.77	0.63	3.22	5.07	4.87	6.94	5.27	8.84	13.87	14	21.84

Example 32

## Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.5% by weight of Compound Q and 0.25% by weight of Compounds D, B, C, E and A. The results show the superiority of hydroxylamines over nitroxides in maintaining a high brightness of the paper upon application and during exposure.

Time in	0.5% Q	0.5% Q	0.5% Q	0.5% Q	0.5% Q	0.5% Q	Blank
Days	0.25% D	0.25% B	0.25% C	0.25% E	0.25% A		

## ISO Brightness

0	78.83	76.96	76.75	78.24	79.85	79.75	78.6
0.75	77.45	77.53	77.15	76.21	78.91	75.36	68.43
1.74	75.77	77.16	76.66	74.36	78.48	72.22	62.89
2.74	73.61	76.59	75.89	72.1	77.7	68.93	58.54
3.75	71.95	75.96	75.21	70.14	77.12	66.09	55.41
6.81	65.96	72.86	72.02	64.11	74.09	58.58	49.29

Example 33

## Accelerated Yellowing with High Intensity Lamps

Additives are added with a sizing treatment on 100% BTMP paper coated with 2 g/m<sup>2</sup>/side using a Pilot Liquid Application System from Bonnier Technology Group Inc. (LAS System). It consists of a hydrophilic roll, soft metering roll, soft backing roll, and sizing pan. A film of sizing solution is drawn through the metering nip onto the hydrophilic roll. The paper gets sized when it runs between the hydrophilic roll and the backing roll.

Starch based coating formulation:

Commercial name	Chemical Nature	Parts
Penford® Gum 280	Hydroxyethylated starch	80
Acronal® S728	N-Butylacrylate & styrene copolymer dispersion	20
Total solids content of 20%, pH around 7.0		

Time in Days	Blank	Sizing only	Sizing 0.36% G 0.84% S	Sizing 0.24% G 0.55% S
PC Number				
0	0	0	0	0
1.01	4.69	4.45	0.59	0.95
1.85	6.78	6.51	0.79	1.53
2.9	8.95	8.98	1.04	1.91
4.1	11.61	10.68	1.41	2.51
4.8	13.29	12.12	1.66	2.84
5.81	14.75	13.98	1.89	3.23
6.77	16.15	15.26	2.04	3.66
7.82	17.16	16.27	2.42	3.85
8.78	18.17	17.19	2.45	4.22
9.89	19.28	18.19	2.66	4.42
10.92	21.11	19.45	3.02	4.97
11.81	20.8	20.31	3.18	5.37
12.81	21.98	21.18	3.55	5.58
13.79	22.68	22.16	3.65	5.99

Example 34

## Accelerated Yellowing with High Intensity Lamps

Additives are added with a pigmented sizing treatment on 100% BTMP paper coated with 2 g/m<sup>2</sup>/side using a Pilot Liquid Application System from Bonnier Technology Group Inc. (LAS System). It consists of a hydrophilic roll, soft metering roll, soft backing roll, and sizing pan. A film of sizing solution is drawn through the metering nip onto the hydrophilic roll. The paper gets sized when it runs between the hydrophilic roll and the backing roll.

100% BTMP paper coated with 4 g/m<sup>2</sup>/side pigments based coating formulation:

Commercial name	Chemical Nature	Parts
Covercarb®	Ultrafine ground calcium carbonate	80
Astraplate®	Delaminated clay	20
Penford® Gum 280	Hydroxyethylated starch	6
Acronal® S728	N-Butylacrylate & styrene copolymer dispersion	12
Sterocoll® AL	Anionic water-in-oil emulsion of an acrylamide-acrylic copolymer	0.1
AZCOTE® 5800M	Ammonium zirconium carbonate solution	0.5
Total solids content of 57%, pH around 8.0		



Time in Days	Blank	Coating only	Coating 0.13% G 0.4% S	Coating 0.4% G 0.74% S	Coating 0.19% G 0.48% S
		PC Number			
0	0	0	0	0	0
1	4.46	3.66	0.65	0.16	0.7
1.83	7.16	5.15	1.03	0.31	1.15
2.91	8.54	6.7	1.21	0.43	1.41
4.11	11.04	8.47	1.53	0.59	1.61
4.8	13.08	10.55	2.1	0.59	1.96
5.82	14.25	11.19	2.02	0.8	2.16
6.78	16.01	12.44	2.39	0.92	2.54
7.83	17.45	13.67	2.61	1.02	2.7
8.8	18.09	14.08	2.68	0.98	2.86
9.9	18.9	14.88	2.95	1.09	3.02
10.94	20.19	15.67	3.12	1.21	3.28
11.81	21.38	16.68	3.59	1.31	3.57
12.82	22.25	17.57	3.58	1.46	3.75
13.8	23.26	18.21	3.83	1.59	4.27

Example 35

Using the accelerated test method, BTMP handsheets containing various combinations of 0.25% by weight of a hindered amine, 0.5% by weight of an s-triazine UV absorber and/or 0.5% by weight of a polymeric additives are compared for efficacy in preventing yellowing. The data are presented on the table below.

Table for Example 35

Square Names	A	B	C	D	E	F	G	H	I	J	K
Days	PC Numbers										
1.14	2.56	1.937	2.557	.1627	.2688	.6753	2.754	1.833	2.188	1.927	5.319
1.97	4.40	3.214	4.042	.4481	.5323	1.249	4.484	2.987	3.643	3.219	8.064
2.98	6.20	4.546	5.752	.7997	.9261	1.873	6.326	4.360	5.338	4.778	10.99
4.06	9.04	6.210	7.590	1.287	1.460	2.742	8.403	5.855	6.964	6.352	13.95
5.03	11.50	8.252	9.841	2.087	2.228	3.957	10.64	7.498	9.008	8.229	17.20
5.98	12.74	9.404	11.19	2.466	2.582	4.593	12.16	8.572	10.13	9.295	19.28
6.96	14.25	10.54	12.58	2.747	2.889	5.203	13.25	9.360	11.04	10.18	21.01
7.98	16.48	12.23	14.65	3.541	3.792	6.425	15.24	11.07	12.66	11.74	23.52

A contains the UV absorber TINUVIN® 400; Compound Y.

B contains the UV absorber TINUVIN® 400 and the polymer PEO.

C contains the UV absorber TINUVIN® 400 and the polymer PTHF.

D contains the hindered amine nitroxide Compound B, the UV absorber TINUVIN® 400 and the polymer PEO.

E contains the hindered amine nitroxide Compound B, the UV absorber TINUVIN® 400 and the polymer PTHF.

F contains the hindered amine nitroxide Compound B and the UV absorber TINUVIN® 400.

G contains the hindered amine nitroxide Compound JJ and the UV absorber TINUVIN® 400.

H contains the hindered amine nitroxide Compound B.

I contains the hindered amine TEMPO.

J contains the hindered amine TEMPO.

K is the control containing no stabilizer additives.

As inspection of the data on the table attests, in best to poorest order  
 $D \approx E > F > H > J > B > I > C > G > A > > K$ . These data show that the combination of a nitroxide, a UV  
 absorber and a polymer coadditive provides the best protection against yellowing after 8 days  
 exposure.

Example 36

Using the accelerated test method, BTMP handsheets containing various combinations of 0.25% by weight of a hindered amine, 0.5% by weight of a benzophenone UV absorber and/or 0.5% by weight of a polymeric additives are compared for efficacy in preventing yellowing. The data are presented on the table below.

Table for Example 36:

Square	A	B	C	D	E	F	G	H	I
Names	PC Numbers								
Days									
.822	1.89	1.545	1.784	.0633	.0881	.0211	1.574	.9791	3.826
1.87	3.41	2.733	3.241	.3018	.2650	.1786	2.911	2.048	6.978
2.91	5.00	4.254	4.939	.6705	.5656	.4648	4.489	3.249	10.19
3.87	6.96	6.038	6.875	1.371	1.183	1.100	6.319	4.770	13.68
4.83	8.59	7.534	8.702	1.808	1.484	1.334	7.759	5.903	16.43
5.81	9.93	8.690	9.944	2.031	1.658	1.483	8.810	6.785	18.26
6.83	11.80	10.37	11.67	2.704	2.217	2.079	10.34	7.968	21.39
7.82	13.59	11.99	13.49	3.288	2.653	2.559	11.53	9.169	23.91

A contains the UV absorber UVINUL® 3000.

B contains the UV absorber UVINUL® 3000 and the polymer PEO.

C contains the UV absorber UVINUL® 3000 and the polymer PTHF.

D contains the hindered amine nitroxide Compound B, the UV absorber UVINUL® 3000 and the polymer PEO.

E contains the hindered amine nitroxide Compound B, the UV absorber UVINUL® 3000 and the polymer PTHF.

F contains the hindered amine nitroxide Compound B and the UV absorber UVINUL® 3000.

G contains the hindered amine Compound JJ and the UV absorber UVINUL® 3000.

H contains the hindered amine nitroxide Compound B.

I is the control containing no stabilizer additives.

As inspection of the data on the table attests, in best to poorest order F>E>D>H>G>B>C≅A>>I.

These data show that the combination of a nitroxide and a benzophenone UV absorber coadditive provides the best protection against yellowing after 8 days exposure.

Example 37

Using the accelerated test method, BTMP handsheets containing various combinations of 0.25% by weight of a hindered amine, 0.5% by weight of a benzophenone UV absorber and/or 0.5% by weight of a polymeric additives are compared for efficacy in preventing yellowing. The data are presented on the table below.

Table for Example 37

Square Names	A	B	C	D	E	F	G
Days	PC Numbers						
1.01	3.60	3.621	1.383	1.764	3.454	1.221	5.048
2.09	6.42	6.027	2.412	3.200	5.842	2.501	8.506
3.05	9.03	8.646	3.845	5.012	8.433	4.123	12.04
4.01	11.60	11.21	4.957	6.360	10.54	5.245	15.26
4.98	13.19	13.01	4.412	7.396	11.92	6.115	17.50
6.01	15.49	15.26	6.252	9.151	14.34	7.611	20.59
7.00	17.75	17.67	7.653	10.83	16.64	8.926	23.32

A contains the UV absorber UVINUL® 3048; Compound Z.

B contains the UV absorber UVINUL® 3048 and the polymer PEO.

C contains the hindered amine nitroxide Compound F, the UV absorber UVINUL® 3048 and the polymer PEO.

D contains the hindered amine nitroxide Compound B and the UV absorber UVINUL® 3048.

E contains the hindered amine Compound JJ and the UV absorber UVINUL® 3048.

F contains the hindered amine nitroxide Compound B.

G is the control containing no stabilizer additives.

As inspection of the data on the table attests, in best to poorest order C>F>D>E>B≡A>>G.

These data show that the combination of a nitroxide, a benzophenone UV absorber and polymer coadditive provides the best protection against yellowing after 7 days exposure.

The tables in Examples 38 to 48 all show PC Numbers.

Example 38

Using the accelerated test method, BTMP handsheets containing various combinations of 1% by weight of a hindered amine, 0.5% by weight of a benzotriazole UV absorber and/or 0.5% by weight of a polymeric additives are compared for efficacy in preventing yellowing. The data are presented on the table below.

Table for Example 38

Days	A	B	C	D	E	F	G	H
0	0	0	0	0	0	0	0	0
1.17	1.62	0.91	1.13	1.4	2.26	2.85	3.35	3.42
2	3	1.81	2.18	2.24	3.69	4.42	5.07	5.26
2.98	4.23	2.62	3.15	3.14	5.21	5.9	6.75	7.22
4	5.67	3.58	4.32	4.44	7.26	7.81	9.09	9.87
5.01	6.73	4.28	5.2	5.13	8.84	9.08	10.48	11.72
5.99	7.73	5.01	5.98	6.08	10.64	10.49	12.11	13.69
6.94	8.75	5.74	6.79	6.75	11.91	11.42	13.29	14.95
7.98	9.62	6.46	7.55	7.48	13.25	12.44	14.36	16.48
8.99	10.27	6.99	8.14	8.2	14.63	13.54	15.66	18.25
9.98	10.6	7.36	8.56	9.03	16.1	14.56	16.81	19.97
11.01	11.34	7.96	9.27	9.93	17.85	15.9	18.37	21.84
12.01	13.48	9.17	10.27	10.57	19.04	16.65	19.19	23.03

- A contains the hindered amine TMHP, the UV absorber TINUVIN® 1130 and the polymer PEO.  
 B contains the hindered amine TMHP, the UV absorber TINUVIN® 1130 and the polymer PTHF.  
 C contains the hindered amine TMHP and the UV absorber TINUVIN® 1130.  
 D contains the hindered amine Compound G and the UV absorber TINUVIN® 1130.  
 E contains the UV absorber TINUVIN® 1130.  
 F contains the hindered amine TMHP.  
 G contains the hindered amine Compound JJ.  
 H is the control containing no stabilizer additives.

As inspection of the data on the table attests, in best to poorest order D>B>C>F>A>E>G>H. These data show that the combination of a hindered amine and a benzotriazole UV absorber coadditive provides the best protection against yellowing after 12 days exposure.

Example 39

Using the ambient test method, BTMP handsheets containing 1%, 0.6% or 0.1% by weight of the hindered amine nitroxide Compound F, 2% by weight of the benzotriazole UV absorber

TINUVIN® 328 and 1% by weight of the polymer PEO are compared for efficacy in preventing yellowing. The data are presented on the table below.

Table for Example 39

Days	p51a	p51b	p51c	p51d	p51e
0	0.00	0.00	0.00	0.00	0.00
1	0.10	-0.08	-0.37	-0.24	-0.21
5	0.54	-0.18	-0.84	-0.64	-0.54
7	1.07	-0.04	-0.67	-0.47	-0.30
8	1.00	-0.12	-0.83	-0.63	-0.42
9	1.37	-0.04	-0.73	-0.50	-0.32
11	1.70	-0.10	-0.97	-0.67	-0.44
13	2.05	-0.08	-0.93	-0.61	-0.40
15	2.33	-0.13	-1.09	-0.73	-0.46
29	4.29	-0.02	-1.12	-0.67	-0.20
40	5.86	0.00	-1.16	-0.69	-0.13
55	7.52	0.03	-1.12	-0.60	0.18
59	7.88	0.02	-1.16	-0.60	0.22
66	8.83	0.05	-1.12	-0.55	0.39
69	9.05	0.01	-1.21	-0.67	0.35
73	9.56	0.09	-1.10	-0.53	0.49
80	10.48	0.14	-1.01	-0.44	0.64
87	10.91	0.10	-1.12	-0.56	0.55
94	12.11	0.28	-0.91	-0.37	0.83
111	13.38	0.32	-0.86	-0.29	1.01
122	14.71	0.52	-0.67	-0.10	1.32
129	14.60	0.37	-0.79	-0.19	1.38
136	15.92	0.50	-0.60	0.17	1.77
143	16.20	0.58	-0.47	0.28	1.99
150	16.68	0.52	-0.52	0.26	2.06
157	17.40	0.61	-0.40	0.34	2.16
164	18.08	0.67	-0.31	0.40	2.41
171	19.54	0.75	-0.13	0.58	2.82
178	19.98	0.89	-0.09	0.63	3.01
185	20.39	0.90	-0.07	0.69	3.23
188	20.70	0.83	-0.02	0.70	3.39
191	21.64	0.92	-0.12	0.66	3.41
199	22.11	0.85	-0.10	0.70	3.52
206	22.94	0.97	-0.02	0.75	3.71
213	23.59	0.91	0.03	0.82	3.82
220	24.34	0.95	-0.02	0.81	3.90

A is the control containing no stabilizer additives.

B is a control which is a Kraft handsheet.

C contains 1% of the nitroxide.

D contains 0.6% of the nitroxide.

E contains 0.1% of the nitroxide.

As inspection of the data on the table attests, in best to poorest order  $C \cong D \cong B > E >> A$ . These data show that the nitroxide provides resistance to yellowing particularly at the 0.6 and 1% by weight levels that makes the color after 220 days of exposure essentially equal to that obtained with Kraft paper. Even at the 0.1% level, the nitroxide provides very good resistance to yellowing.

#### Example 40

Using the accelerated test method; the ambient test method; and dark aging, BTMP handsheets containing 0.25%, 0.2%, 0.15%, 0.1% or 0.05% by weight of the hindered amine nitroxide Compound F are compared for efficacy in preventing yellowing. The data are presented on the three tables below respectively.

#### Accelerated Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
24.33	2.27	2.55	3.16	3.46	3.68	5.18
48.50	4.17	4.52	5.46	6.05	6.29	8.60
73.25	5.71	6.18	7.46	8.05	8.62	11.65
97.00	7.42	7.94	9.39	10.34	10.97	14.68
121.50	9.00	9.57	11.42	12.57	13.17	17.34
144.50	10.56	11.28	13.32	14.53	15.36	20.05
168.25	12.04	12.84	15.08	16.52	17.39	22.57

## Ambient Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
3.02	0.39	0.21	0.39	0.49	0.44	0.80
10.01	1.00	0.63	1.01	1.23	1.27	2.04
17.00	1.33	0.90	1.44	1.78	1.82	3.01
31.03	1.97	1.44	2.43	2.88	3.09	5.04
38.06	2.71	1.98	3.18	3.73	4.04	6.34
45.15	3.24	2.50	3.84	4.48	4.80	7.33
52.15	3.59	2.77	4.22	4.94	5.37	8.00
55.02	3.60	2.72	4.22	4.99	5.49	8.21
62.02	4.31	3.28	5.04	5.91	6.36	9.28
66.00	4.49	3.38	5.27	6.03	6.63	9.78

## Dark Aging Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
3.06	0.18	0.12	0.16	0.19	0.17	0.18
10.04	0.23	0.18	0.21	0.23	0.22	
21.02	0.16	0.13	0.16	0.19	0.19	0.31
24.17	0.23	0.18	0.21	0.26	0.25	0.41
38.16	0.16	0.12	0.15	0.21	0.23	0.48
45.15	0.21	0.17	0.21	0.27	0.28	0.57
52.01	0.20	0.15	0.19	0.25	0.26	0.58
62.96	0.20	0.15	0.21	0.27	0.28	0.67

A contains 0.25% of the nitroxide.

B contains 0.2% of the nitroxide.

C contains 0.15% of the nitroxide.



D contains 0.1% of the nitroxide.

E contains 0.05% of the nitroxide.

F is a control containing no stabilizer additive.

During accelerated photoaging, inspection of the data on the table shows in best to poorest order A>B>C>D>E>F. These data show that the nitroxide provides resistance to yellowing after 168 hours of accelerated photoaging.

During ambient photoaging, inspection of the data on the table shows in best to poorest order B>A>C>D>E>>F. These data show that the nitroxide provides resistance to yellowing after 66 days of ambient photoaging.

During dark aging, inspection of the data on the table shows in best to poorest order B>C>A>D>E>>F. These data show that the nitroxide provides resistance to yellowing after 63 days of dark aging.

#### Example 41

Using the accelerated test method; the ambient test method; and dark aging, BTMP handsheets containing 0.25% by weight of the hindered amine nitroxide Compound F and 1%, 0.5%, 0.25%, 0.2% or 0.1% by weight of the benzotriazole UV absorber TINUVIN® 1130 are compared for efficacy in preventing yellowing. The data are presented on the three tables below respectively.

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
24.50	0.28	0.53	1.14	1.30	1.88	5.39
49.25	0.57	0.93	1.96	2.35	3.38	8.92
72.55	0.86	1.46	2.84	3.44	4.83	12.23
97.50	1.20	1.92	3.66	4.57	6.35	15.14
120.50	1.66	2.54	4.72	5.87	7.97	18.18
144.25	2.02	3.06	5.56	6.98	9.39	20.82
168.50	2.57	3.73	6.71	8.34	11.05	23.47

## Ambient Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.02	0.09	-0.03	0.03	-0.02	0.00	0.41
9.01	0.42	0.26	0.42	0.36	0.49	1.75
16.00	0.48	0.22	0.45	0.51	0.72	2.75
23.02	0.58	0.38	0.73	0.79	1.05	3.90
30.05	0.64	0.43	0.95	0.99	1.31	4.79
37.07	0.94	0.71	1.34	1.41	1.84	6.17
44.15	1.11	0.96	1.72	1.76	2.27	7.26
51.15	1.20	1.04	1.87	1.94	2.55	7.98
54.03	1.31	1.09	1.95	1.96	2.54	8.27
61.02	1.49	1.29	2.35	2.35	3.04	9.29
64.98	1.44	1.33	2.43	2.38	3.14	9.73

## Dark Aging Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.06	0.05	0.02	-0.01	-0.01	0.00	0.02
9.04	0.12	0.10	0.05	0.06	0.08	0.15
20.02	0.05	0.01	-0.03	-0.03	0.00	0.13
23.17	0.15	0.07	0.03	0.06	0.05	0.21
30.17	0.06	0.00	-0.04	-0.05	-0.03	0.20
37.17	0.10	0.00	-0.02	-0.04	0.00	0.26
44.15	0.13	0.08	0.00	0.03	0.06	0.33
51.06	0.15	0.03	-0.01	0.00	0.04	0.37
61.96	0.14	0.01	-0.01	-0.01	0.05	0.43
79.06	0.30	0.07	0.08	0.01	0.13	0.51

- A contains 1% of the UV absorber.
- B contains 0.5% of the UV absorber.
- C contains 0.25% of the UV absorber.
- D contains 0.2% of the UV absorber.
- E contains 0.1% of the UV absorber.
- F is a control containing no stabilizer additive.

During accelerated photoaging, inspection of the data on the table shows in best to poorest order A>B>C>D>E>>F. These data show that the nitroxide plus UV absorber provides resistance to yellowing after 168 hours of accelerated photoaging.

During ambient photoaging, inspection of the data on the table shows in best to poorest order B>A>C>D>E>>F. These data show that the nitroxide plus UV absorber provides resistance to yellowing after 65 days of ambient photoaging.

During dark aging, inspection of the data on the table shows in best to poorest order D>B>C>E>A>F. These data show that the nitroxide plus UV absorber provides resistance to yellowing after 79 days of dark aging, but that in the dark the UV absorber is much less critical for efficacy.

#### Example 42

Using the accelerated test method; the ambient test method; and dark aging, BTMP handsheets containing 0.25% by weight of the hindered amine nitroxide Compound B and 1%, 0.75%, 0.5%, 0.25% or 0.1% by weight of the polymer PTHF are compared for efficacy in preventing yellowing. The data are presented on the three tables below respectively.

## Accelerated Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
25.00	1.42	1.08	1.50	1.58	1.57	4.56
48.75	2.41	1.98	2.64	2.82	2.86	7.58
73.25	3.63	3.07	4.04	4.37	4.46	11.08
96.25	4.88	4.12	5.38	5.78	5.95	14.07
120.00	5.90	5.14	6.62	7.20	7.41	16.88
144.25	7.20	6.22	8.14	8.64	8.84	19.74

## Ambient Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
8.00	0.37	0.24	0.17	0.41	0.45	1.66
14.99	0.39	0.32	0.38	0.56	0.73	2.74
22.01	0.59	0.55	0.66	0.96	1.10	3.90
29.02	0.78	0.74	0.85	1.25	1.42	4.88
36.07	1.21	1.13	1.24	1.50	2.06	6.21
50.14	1.59	1.44	1.66	2.33	2.57	7.93
53.01	1.66	1.51	1.73	2.37	2.65	8.16
60.01	2.06	1.76	2.13	2.90	3.16	9.22
63.97	2.03	1.81	2.16	3.05	3.36	9.73
70.99	2.29	2.07	2.60	3.55	3.89	10.75
77.97	2.55	2.27	2.81	3.85	4.31	11.64

## Dark Aging Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.05	-0.12	-0.13	-0.10	-0.09	-0.08	-0.06
8.03	-0.12	-0.10	-0.07	-0.09	-0.08	0.05
19.01	-0.19	-0.18	-0.15	-0.18	-0.17	0.02
22.16	-0.13	-0.12	-0.10	-0.10	-0.10	0.10
29.16	-0.23	-0.21	-0.22	-0.19	-0.21	0.08
36.16	-0.21	-0.17	-0.16	-0.17	-0.19	0.17
50.05	-0.21	-0.16	-0.15	-0.17	-0.19	0.28

A contains 1% of the polymer PTHF.

B contains 0.75% of the polymer PTHF.

C contains 0.5% of the polymer PTHF.

D contains 0.25% of the polymer PTHF.

E contains 0.1% of the polymer PTHF.

F is a control containing no stabilizer additive.

During accelerated photoaging, inspection of the data on the table shows in best to poorest order B>A>C>D>E>>F. These data show that the nitroxide plus polymer provides resistance to yellowing after 144 hours of accelerated photoaging.

During ambient photoaging, inspection of the data on the table shows in best to poorest order B>A>C>D>E>>F. These data show that the nitroxide plus polymer provides resistance to yellowing after 78 days of ambient photoaging.

During dark aging, inspection of the data on the table shows in best to poorest order A>E>D>B>C>>>F. These data show that the nitroxide plus polymer provides resistance to yellowing after 50 days of dark aging.

Example 43

Using the accelerated test method; the ambient test method; and dark aging, BTMP handsheets containing 0.25% by weight of the hindered amine nitroxide Compound B, 1%, 0.5%, 0.25%, 0.2% or 0.1% by weight of the benzotriazole UV absorber TINUVIN® 1130 and 0.5% by weight of polymer PTHF are compared for efficacy in preventing yellowing. The data are presented on the three tables below respectively.

Accelerated Test Method						
Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
23.42	-0.01	0.48	0.60	0.47	1.34	4.52
47.25	0.34	1.22	1.32	1.18	2.65	8.11
71.75	0.71	1.91	2.00	1.80	3.81	11.04
96.17	1.04	2.62	2.72	2.49	4.90	13.60
119.75	1.64	3.42	3.51	3.28	6.40	16.52
145.75	2.30	5.05	5.11	4.65	8.26	20.82
168.08	2.73	5.60	5.59	5.22	9.24	22.57

Ambient Test Method						
Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
6.98	-0.14	0.20	-0.01	0.07	0.48	1.79
13.97	-0.11	0.35	0.04	0.21	0.48	2.63
20.99	-0.04	0.58	0.25	0.44	0.74	3.73
28.01	0.02	0.71	0.37	0.63	1.01	4.73
35.04	0.24	1.06	0.64	0.98	1.41	6.01
42.11	0.47	1.28	0.91	1.26	1.79	7.02
49.11	0.55	1.29	0.88	1.36	1.87	7.78
51.99	0.61	1.33	0.95	1.45	1.91	8.07
59.11	0.79	1.70	1.24	1.72	2.40	9.32
62.97	0.76	1.78	1.25	1.77	2.52	9.70
69.97	1.16	2.09	1.59	2.14	3.00	10.88
77.01	1.25	2.27	1.64	2.30	3.27	11.75

## Dark Aging Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
6.97	0.00	0.04	0.03	0.04	0.10	0.17
17.95	-0.09	-0.03	-0.05	-0.01	0.01	0.16
21.09	-0.04	-0.03	-0.01	0.02	0.06	0.23
28.10	-0.12	-0.16	-0.10	-0.07	-0.04	0.19
35.10	-0.07	-0.10	-0.07	-0.02	-0.02	0.28
48.99	-0.05	-0.08	-0.05	-0.02	0.00	0.36
59.89	-0.07	-0.11	-0.06	-0.04	-0.01	0.45

A contains 1% of the UV absorber.

B contains 0.5% of the UV absorber.

C contains 0.25% of the UV absorber.

D contains 0.2% of the UV absorber.

E contains 0.1% of the UV absorber.

F is a control containing no stabilizer additive.

During accelerated photoaging, inspection of the data on the table shows in best to poorest order A>D>B>C>E>>F. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 168 hours of accelerated photoaging.

During ambient photoaging, inspection of the data on the table shows in best to poorest order A>C>D=B>E>>F. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 77 days of ambient photoaging.

During dark aging, inspection of the data on the table shows in best to poorest order B>A>C>D>E>F. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 60 days of dark aging.

Example 44

Using the accelerated test method; the ambient test method; and dark aging, BTMP handsheets containing 0.25%, 0.2%, 0.15%, 0.1% and 0.05% by weight of the hindered amine nitroxide Compound B, 0.5% by weight of the benzotriazole UV absorber TINUVIN® 1130 and 0.5% by weight of polymer PTHF are compared for efficacy in preventing yellowing. The data are presented on the three tables below respectively.

## Accelerated Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
26.00	0.49	0.41	1.12	1.93	2.02	6.01
48.33	1.10	0.91	1.95	3.21	3.33	9.20
73.50	1.63	1.39	2.73	4.47	4.55	11.87
96.00	2.23	1.80	3.32	5.44	5.59	14.00
119.83	2.64	2.31	4.13	6.63	6.65	15.98
144.83	3.16	2.76	4.81	7.70	7.64	17.94
167.67	3.76	3.36	5.63	8.85	8.82	19.87
191.00	4.25	3.73	6.15	9.86	9.64	21.07
216.42	5.20	4.73	7.58	11.69	11.18	23.66



## Ambient Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.99	-0.19	-0.10	-0.12	0.10	0.20	0.76
8.98	-0.17	0.06	0.01	0.37	0.61	1.98
16.00	-0.08	0.17	0.22	0.70	1.09	3.14
23.03	0.09	0.28	0.31	0.93	1.45	3.98
30.07	0.31	0.58	0.65	1.39	2.03	5.30
37.13	0.56	0.80	0.99	1.85	2.47	6.30
44.04	0.61	0.86	1.00	1.96	2.83	7.10
47.00	0.71	0.94	1.02	2.02	2.94	7.26
54.00	0.93	1.18	1.35	2.36	3.47	8.36
57.96	0.93	1.20	1.46	2.48	3.63	8.86
64.98	1.14	1.43	1.79	2.76	4.03	9.95
72.00	1.27	1.75	2.04	3.21	4.61	11.01

## Dark Aging Test Method

Time	a	b	c	d	e	f
0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.02	0.03	0.03	0.06	0.04	0.07	0.11
12.98	-0.06	-0.06	0.00	-0.01	0.02	0.21
16.15	-0.01	-0.01	0.03	0.03	0.07	0.28
23.15	-0.09	-0.12	-0.05	-0.07	0.02	0.25
30.15	-0.10	-0.08	-0.03	-0.07	0.05	0.34
37.13	-0.06	-0.06	-0.01	-0.01	0.08	0.38
44.04	-0.09	-0.06	-0.03	-0.02	0.07	0.42
54.94	-0.11	-0.07	-0.03	-0.05	0.08	0.47
72.03	0.00	-0.04	0.00	-0.03	0.11	0.56

A contains 0.25% of the nitroxide.

B contains 0.2% of the nitroxide.

C contains 0.15% of the nitroxide.

D contains 0.1% of the nitroxide.

E contains 0.05% of the nitroxide.

F is a control containing no stabilizer additive.

During accelerated photoaging, inspection of the data on the table shows in best to poorest order B>A>C>D>E>>F. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 216 hours of accelerated photoaging.

During ambient photoaging, inspection of the data on the table shows in best to poorest order A>B>C>D>E>>F. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 72 days of ambient photoaging.

During dark aging, inspection of the data on the table shows in best to poorest order B>D>C>A>E>>F. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 72 days of dark aging.

#### Example 45

Using the accelerated test method; the ambient test method; and dark aging, BTMP handsheets containing 0.25% by weight of the hindered amine nitroxide Compound B, 0.5% by weight of the benzotriazole UV absorber TINUVIN® 1130 and 1%, 0.75%, 0.25% or 0.1% by weight of the polymer PTHF are compared for efficacy in preventing yellowing. The data are presented on the three tables below respectively.

## Accelerated Test Method

Time	a	b	c	d	e
0.00	0.00	0.00	0.00	0.00	0.00
22.33	0.49	0.86	0.31	0.45	4.68
47.50	1.11	1.76	0.77	1.04	7.82
70.00	1.61	2.53	1.20	1.49	10.05
93.00	2.26	3.36	1.73	2.08	12.46
118.83	2.70	4.10	2.16	2.67	14.44
141.67	3.41	5.04	2.80	3.39	16.69
165.00	3.95	5.74	3.20	3.90	18.16
189.42	4.97	7.28	4.18	5.52	21.00
214.00	6.32	9.24	5.37	6.86	24.13

## Ambient Test Method

Time	a	b	c	d	e
0.00	0.00	0.00	0.00	0.00	0.00
7.90	-0.21	0.13	-0.20	-0.07	1.75
14.92	-0.10	0.32	-0.08	0.12	2.96
21.92	-0.05	0.43	-0.06	0.21	3.87
28.98	0.24	0.74	0.19	0.52	5.15
43.04	0.59	1.03	0.29	1.08	6.97
45.91	0.69	1.08	0.35	0.99	7.13
52.88	0.90	1.40	0.55	1.26	8.23
56.92	0.90	1.46	0.59	1.34	8.74
63.90	1.12	1.78	0.85	1.71	9.77

## Dark Aging Test Method

Time	a	b	c	d	e
0.00	0.00	0.00	0.00	0.00	0.00
0.94	0.04	0.03	0.02	0.02	0.04
11.92	-0.03	-0.04	-0.06	-0.04	0.23
15.06	0.03	0.00	-0.01	0.01	0.33
22.07	-0.07	-0.07	-0.09	-0.09	0.31
29.07	-0.04	-0.04	-0.08	-0.04	0.42
42.96	-0.03	-0.04	-0.06	-0.05	0.49
53.85	-0.01	-0.04	-0.07	-0.05	0.61
70.96	0.06	0.01	-0.03	-0.04	0.70

A contains 1% of the polymer PTHF.

B contains 0.75% of the polymer PTHF.

C contains 0.25% of the polymer PTHF.

D contains 0.1% of the polymer PTHF.

E is a control containing no stabilizer additive.

During accelerated photoaging, inspection of the data on the table shows in best to poorest order C>A>D>B>>>E. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 214 hours of accelerated photoaging.

During ambient photoaging, inspection of the data on the table shows in best to poorest order C>A>D>B>>>E. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 64 days of ambient photoaging.

During dark aging, inspection of the data on the table shows in best to poorest order D>C>B>A>>>E. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 71 days of dark aging.

Example 46

Using the accelerated test method; the ambient test method; and dark aging, BCTMP Aspen handsheets containing 0.25% by weight of the hindered amine nitroxide Compound B, 1%, 0.5% or 0% by weight of the benzotriazole UV absorber TINUVIN® 1130 and 1%, 0.5% or 0% by weight of the polymer PTHF are compared for efficacy in preventing yellowing. The data are presented on the three tables below respectively.

## Accelerated Test Method

Time	a	b	c	d	e
0.00	0.00	0.00	0.00	0.00	0.00
1.00	3.50	2.59	0.77	1.02	5.81
2.02	5.57	3.81	1.16	1.51	8.77
3.03	7.49	5.05	1.71	2.02	11.62
4.01	9.04	5.82	2.06	2.46	13.93
4.98	10.54	6.76	2.56	2.95	16.26
6.14	12.04	7.67	2.82	3.21	18.49
7.64	13.90	8.61	3.37	3.81	21.64
8.24	14.60	8.76	3.54	3.95	22.42

## Ambient Test Method

Time	a	b	c	d	e
0.00	0.00	0.00	0.00	0.00	0.00
1.99	0.76	0.49	0.07	0.26	1.51
3.06	1.27	0.84	0.28	0.48	2.44
24.13	1.80	1.22	0.52	0.73	3.25
31.13	2.00	1.34	0.61	0.76	3.85
34.02	1.94	1.33	0.61	0.79	3.93
41.00	2.16	1.63	0.84	0.95	4.63
45.00	2.39	1.66	0.84	0.96	4.91
52.14	2.81	1.66	1.04	1.13	5.57
59.02	3.15	1.84	1.23	1.22	6.10

## Dark Aging Test Method

Time	a	b	c	d	e
0.00	0.00	0.00	0.00	0.00	0.00
9.17	-0.04	-0.03	0.01	-0.02	0.01
16.16	0.03	0.01	0.07	0.04	0.03
23.13	0.09	0.08	0.12	0.08	0.10
30.06	0.07	0.03	0.10	0.03	0.05
40.94	0.06	0.04	0.11	0.05	0.05
58.04	0.11	0.28	0.32	0.28	0.29

A contains no UV absorber or no polymer PTHF.

B contains no UV absorber and 1% of the polymer PTHF.

C contains of 1% of the UV absorber and no polymer PTHF.

D contains 0.5% of the UV absorber and 0.5% of polymer PTHF.

E is a control containing no stabilizer additive.

During accelerated photoaging, inspection of the data on the table shows in best to poorest order C>D>B>A>>E. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 8 days of accelerated photoaging.

During ambient photoaging, inspection of the data on the table shows in best to poorest order C>D>B>A>>E. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 59 days of ambient photoaging.

During dark aging, inspection of the data on the table shows in best to poorest order A>B>D>E>C. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 71 days of dark aging.

Example 47

Using the accelerated test method; the ambient test method; and dark aging, stone-ground wood (SGW) handsheets containing 0.25% by weight of the hindered amine nitroxide Compound B, 1%, 0.5% or 0% by weight of the benzotriazole UV absorber TINUVIN® 1130 and 1%, 0.5% or 0% by weight of the polymer PTHF are compared for efficacy in preventing yellowing. The data are presented on the three tables below respectively.

## Accelerated Test Method

Time	a	b	c	d	e
0.00	0.00	0.00	0.00	0.00	0.00
0.99	3.94	3.28	0.82	1.51	8.19
1.97	6.95	5.11	1.69	2.70	12.54
2.94	9.75	6.84	2.48	3.81	16.70
4.09	12.18	8.83	3.34	5.09	20.41
5.60	15.07	10.72	4.42	6.39	25.36
6.20	15.74	11.24	4.83	6.90	26.84

## Ambient Test Method

Time	a	b	c	d	e
0.00	0.00	0.00	0.00	0.00	0.00
6.95	0.44	0.15	-0.25	-0.24	1.80
14.01	1.19	0.63	0.08	0.03	3.22
28.08	2.27	1.28	0.51	0.36	5.25
30.98	2.26	1.32	0.57	0.38	5.30
37.96	2.91	1.74	0.82	0.63	6.55
41.94	3.03	1.86	0.89	0.70	7.13
48.99	3.64	2.12	1.21	0.83	8.30
55.98	4.12	2.40	1.44	1.01	9.15

## Dark Aging Test Method

Time	a	b	c	d	e
0.00	0.00	0.00	0.00	0.00	0.00
7.13	-0.08	-0.17	-0.06	-0.13	-0.10
14.12	-0.01	-0.15	-0.01	-0.14	-0.02
21.08	0.16	0.02	0.10	0.00	0.18
28.02	0.13	-0.02	0.09	-0.03	0.13
38.90	0.18	0.00	-0.03	-0.09	0.13
56.00	0.88	0.13	0.31	0.05	0.28

A contains no UV absorber or no polymer PTHF.

B contains no UV absorber and 1% of the polymer PTHF.

C contains of 1% of the UV absorber and no polymer PTHF.

D contains 0.5% of the UV absorber and 0.5% of polymer PTHF.

E is a control containing no stabilizer additive.

During accelerated photoaging, inspection of the data on the table shows in best to poorest order C>D>B>A>>E. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 6 days of accelerated photoaging.

During ambient photoaging, inspection of the data on the table shows in best to poorest order D>C>B>A>>E. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 56 days of ambient photoaging.

During dark aging, inspection of the data on the table shows in best to poorest order D>B>E>C>A. These data show that the nitroxide plus UV absorber plus polymer provides resistance to yellowing after 56 days of dark aging.



Example 48

Using the accelerated test method; the ambient test method; and dark aging, BTMP paper loadings with 0.25%, 0.2%, 0.15%, 0.1% and 0.05% by weight of hindered amine nitroxide Compound B and 0.5% by weight of Compound LL are compared for efficacy in preventing yellowing on aging. The data are presented on the three tables below respectively.

## Accelerated Test Method

Time	a	b	c	d	e	f	g	h
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24.67	2.94	2.72	3.19	3.46	4.29	4.76	6.70	6.48
48.25	5.79	5.16	5.68	6.06	7.46	8.16	10.98	10.98
71.75	7.60	7.25	7.93	8.31	10.03	11.02	14.43	14.37
97.08	9.13	8.83	9.60	10.13	11.85	13.14	16.98	17.00
120.25	10.76	10.55	11.21	11.72	13.58	15.01	19.31	19.34
168.25	14.63	14.71	15.17	15.52	18.08	19.76	25.10	25.36

## Ambient Test Method

Time	a	b	c	d	e	f	g	h
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8.01	0.39	0.21	0.54	0.50	0.68	1.13	1.91	2.05
15.03	0.62	0.41	0.81	0.80	1.05	1.67	2.80	3.02
22.05	1.19	0.89	1.30	1.28	1.62	2.44	3.92	4.31
29.14	1.74	1.25	1.74	1.78	2.13	3.17	4.88	5.38
36.14	2.07	1.45	2.00	2.00	2.48	3.56	5.65	6.25
39.01	2.03	1.47	2.01	2.06	2.50	3.60	5.75	6.46
46.01	2.46	1.98	2.53	2.53	3.11	4.42	6.82	7.62
50.01	2.62	2.04	2.67	2.71	3.31	4.74	7.28	8.10
56.99	3.06	2.40	3.09	3.11	3.71	5.33	8.24	9.17
64.01	3.36	2.80	3.46	3.42	4.25	5.94	9.19	10.03

## Dark Aging Test Method

Time	a	b	c	d	e	f	g	h
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8.16	0.09	-0.06	0.02	0.08	0.02	0.05	0.13	0.17
15.17	-0.08	-0.21	-0.11	-0.05	-0.07	-0.05	0.10	0.18
22.18	-0.13	-0.22	-0.17	-0.11	-0.09	-0.07	0.13	0.30
29.14	0.01	-0.16	0.01	0.06	0.01	0.06	0.29	0.40
36.07	0.00	-0.22	-0.05	0.02	-0.02	0.03	0.27	0.40
46.95	-0.07	-0.21	-0.05	0.01	-0.03	0.04	0.32	0.49

A contains 0.25% nitroxide and 0.5% brightner.

B contains 0.25% nitroxide and no brightner.

C contains 0.2% nitroxide and 0.5% brightner.

D contains 0.15% nitroxide and 0.5% brightner.

E contains 0.1% nitroxide and 0.5% brightner.

F contains 0.05% nitroxide and 0.5% brightner.

G is a control containing no nitroxide and 0.5% brightner.

H is a control containing no stabilizer additive.

During accelerated photoaging, inspection of the data on the table shows in best to poorest order A>B>C>D>E>F>>G=H. These data show that the nitroxide plus brightner provides resistance to yellowing after 168 hours of accelerated photoaging.

During ambient photoaging, inspection of the data on the table shows in best to poorest order B>A=C=D>E>F>G>H. These data show that the nitroxide plus brightner provides resistance to yellowing after 64 days of ambient photoaging.

During dark aging, inspection of the data on the table shows in best to poorest order B>C>A>E>D>F>G>H. These data show that the nitroxide plus brightner provides resistance to yellowing after 47 days of dark aging.

Example 49

Using the dark aging method, BTMP handsheets are allowed to sit in the dark for 10 days before treatment with 0.05% by weight of nitroxide Compound B. The sheets are then dark aged for a period of 72 days. The ISO brightness data are given on the table below.

Days	e	f
-10	78.11	78.22
0	77.94	77.48
2.02	77.71	77.14
12.98	77.89	76.85
16.15	77.72	76.65
23.15	77.87	76.75
30.15	77.8	76.48
37.13	77.68	76.37
44.04	77.74	76.28
54.94	77.7	76.13
72.03	77.6	75.89

E contains 0.05% nitroxide.

F is a control containing no stabilizer additive.

The nitroxide provides the good ISO brightness values after the 72 day period of dark aging.

Example 50**Accelerated Yellowing with High Intensity Lamps**

BTMP sheets are treated with 0.5% by weight of Compound S and 0.5% by weight of Compound A and Compound FF

Time in days	S, A	S, FF	S	A	FF	Control
PC Number						
0	0	0	0	0	0	0
0.78	0.14	-0.23	1.93	0.7	0.67	3.26
1.75	0.38	-0.32	3.77	1.12	1.09	6.19
2.75	0.85	-0.19	5.8	1.93	1.86	9.16
3.77	1.25	-0.14	7.62	2.51	2.45	11.6
4.77	1.54	-0.22	9.48	3.19	3.07	13.8
5.75	1.87	-0.07	10.9	3.74	3.59	15.83
6.78	2.16	-0.13	11.87	4.22	4.07	16.97

Inspection of the data reveals that hydroxylamine citrate salt are more effective in inhibiting yellowing than the hydroxylamine and in combination with a UVA superior results are achieved with the citrate salt.

#### Example 51

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound A and with 1% by weight of the sulfur containing inhibitors:

2-(2'-methoxyethoxy)-ethanethiol;  
2,2'-oxydiethanethiol;  
1-thioglycerol;  
sodium thioglycolate;  
thiolactic acid;  
sodium thiolactate;  
 $\beta$ -mercaptopropionic acid;  
sodium  $\beta$ -mercaptopropionate;

glycol dimercaptoacetate;  
glycol dimercaptopropionate;  
polyethylene glycol dimercaptoacetate;  
polyethylene glycol dimercaptopropionate;  
pentaerythritol tetrathioglycolate;  
trimethylol propane tri-(3-mercaptopropionate);  
polymethylene sulfide;  
disodium methylene bis thiopropionate;  
3,3'-thiodipropionic acid;  
dithiothreitol.

The sheets treated with a combination of hydroxylamine and sulfur containing compounds exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of hydroxylamine and sulfur containing compounds are used.

#### Example 52

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound FF and with 1% by weight of the sulfur containing inhibitors:

2-(2'-methoxyethoxy)-ethanethiol;  
2,2'-oxydiethanethiol;  
1-thioglycerol;  
sodium thioglycolate;  
thiolactic acid;  
sodium thiolactate;  
 $\beta$ -mercaptopropionic acid;  
sodium  $\beta$ -mercaptopropionate;

glycol dimercaptoacetate;  
glycol dimercaptopropionate;  
polyethylene glycol dimercaptoacetate;  
polyethylene glycol dimercaptopropionate;  
pentaerythritol tetrathioglycolate;  
trimethylol propane tri-(3-mercaptopropionate);  
polymethylene sulfide;  
disodium methylene bis thiopropionate;  
3,3'-thiodipropionic acid;  
dithiothreitol.

The sheets treated with a combination of hydroxylamine salt and sulfur containing compounds exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of hydroxylamine salt and sulfur containing compounds are used.

#### Example 53

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound B and with 1% by weight of the sulfur containing inhibitors Compounds GG, HH and II

Time in Days	B,GG	B,HH	B,II	GG	HH	II	control
PC Number							
0	0	0	0	0	0	0	0
0.92	1.1	1.25	1.1	2.92	3.65	2.55	3.94
1.88	2.4	2.32	2.09	5.9	6.45	4.93	6.91
3.9	5.33	4.36	3.98	11.88	11.48	9.81	12.15
5	7.31	5.59	5.13	15.56	14.26	12.86	14.84
5.98	9.37	6.88	6.32	18.55	16.58	15.5	17.13
6.95	11.32	8.06	7.37	21.3	18.51	17.75	18.93
7.92	13.34	9.17	8.55	24.39	20.74	20.43	21.43
8.88	15.1	10.34	9.72	27.33	22.74	22.9	23.55

The sheets treated with a combination of nitroxide and sulfur containing compounds exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxides and sulfur containing compounds are used. Inspection of the data reveals that Compound HH and II are particularly effective when combined with a nitroxide.

#### Example 54

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound A, 0.5% of Compound R and with 1% by weight of the sulfur containing inhibitors:

2-(2'-methoxyethoxy)-ethanethiol;

2,2'-oxydiethanethiol;

1-thioglycerol;

sodium thioglycolate;

thiolactic acid;  
sodium thiolactate;  
 $\beta$ -mercaptopropionic acid;  
sodium  $\beta$ -mercaptopropionate;  
glycol dimercaptoacetate;  
glycol dimercaptopropionate;  
polyethylene glycol dimercaptoacetate;  
polyethylene glycol dimercaptopropionate;  
pentaerythritol tetrathioglycolate;  
trimethylol propane tri-(3-mercaptopropionate);  
polymethylene sulfide;  
disodium methylene bis thiopropionate;  
3,3'-thiodipropionic acid;  
dithiothreitol.

The sheets treated with a combination of hydroxylamine, UVA and sulfur containing compounds exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of hydroxylamine, UVA and sulfur containing compounds are used.

#### Example 56

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound FF, 0.5% of Compound R and with 1% by weight of the sulfur containing inhibitors:

2-(2'-methoxyethoxy)-ethanethiol;  
2,2'-oxydiethanethiol;  
1-thioglycerol;  
sodium thioglycolate;



thiolactic acid;  
sodium thiolactate;  
 $\beta$ -mercaptopropionic acid;  
sodium  $\beta$ -mercaptopropionate;  
glycol dimercaptoacetate;  
glycol dimercaptopropionate;  
polyethylene glycol dimercaptoacetate;  
polyethylene glycol dimercaptopropionate;  
pentaerythritol tetrathioglycolate;  
trimethylol propane tri-(3-mercaptopropionate);  
polymethylene sulfide;  
disodium methylene bis thiopropionate;  
3,3'-thiodipropionic acid;  
dithiothreitol.

The sheets treated with a combination of hydroxylamine salt, UVA and sulfur containing compounds exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of hydroxylamine salt, UVA and sulfur containing compounds are used.

#### Example 57

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound B, 0.5% of Compound R and with 1% by weight of the sulfur containing inhibitors Compounds GG, HH and II

Time in Days	R	B	R,B,G G	R,B, HH	R,B, II	R,GG	R,HH	R,II	control
PC Number									
0	0	0	0	0	0	0	0	0	0
0.92	1.62	1.52	0.97	0.48	0.5	1.58	1.92	1.51	3.94
1.88	3.05	3	2.08	1.1	1.2	3.23	3.56	3.08	6.91
3.9	5.8	5.99	4.33	2.14	2.55	6.65	6.75	6.35	12.15
5	7.47	7.58	5.82	2.99	3.65	9.12	8.93	8.63	14.84
5.98	9.07	9	7.26	3.82	4.7	11.17	10.65	10.59	17.13
6.95	10.28	10.35	8.43	4.58	5.78	12.99	12.25	12.36	18.93
7.92	11.58	11.72	10.03	5.38	6.77	14.95	14.05	14.36	21.43
8.88	12.9	12.88	11.21	6.13	7.89	17.25	15.97	16.12	23.55

The sheets treated with a combination of nitroxide, UVA and sulfur containing compounds exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxides, UVA and sulfur containing compounds are used. Inspection of the data reveals that Compound HH and II are particularly effective when combined with a nitroxide and UVA.

#### Example 58

#### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound A and with 1% by weight of the following metal salts:



The sheets treated with a combination of hydroxylamine and metal salt exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of hydroxylamine and metal salt are used.

#### Example 59

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound B and with 1% by weight of the following metal salts:

MgSO<sub>4</sub>

MnSO<sub>4</sub>

ZnSO<sub>4</sub>

The sheets treated with a combination of nitroxide and metal salt exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and metal salt are used.

#### Example 60

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound A and with 1% by weight of the diene compounds:

1-methoxy-1,3-cyclohexadiene;

1-methoxy-1,4-cyclohexadiene;

2,4-hexadienoic acid;

trans, trans-2,4-hexadien-1-ol.

The sheets treated with a combination of hydroxylamine and diene compound exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the

performance enhancement when combinations of hydroxylamine and diene compound are used.

#### Example 61

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound B and with 1% by weight of the following diene compounds:

1-methoxy-1,3-cyclohexadiene;  
1-methoxy-1,4-cyclohexadiene;  
2,4-hexadienoic acid;  
trans, trans-2,4-hexadien-1-ol.

The sheets treated with a combination of nitroxide and diene compound exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of nitroxide and compounds are used.

#### Example 62

##### Accelerated Yellowing with High Intensity Lamps

BTMP sheets are treated with 0.25% by weight of Compound FF and with 1% by weight of the following diene compounds:

1-methoxy-1,3-cyclohexadiene;  
1-methoxy-1,4-cyclohexadiene;  
2,4-hexadienoic acid;  
trans, trans-2,4-hexadien-1-ol.

The sheets treated with a combination of hydroxylamine salt and diene compound exhibit substantial inhibition to yellowing compared to the untreated control sheet and illustrate the performance enhancement when combinations of hydroxylamine salt and compounds are used.

#### Example 63

##### 1-Oxyl-2,2,6,6-tetramethyl-4-glycidyloxypiperidine

A vigorously stirred two phase solution of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, epichlorohydrin, tetrabutylammonium bromide in 50% aqueous sodium hydroxide and toluene is reacted together. The organic phase is dried over anhydrous magnesium sulfate and concentrated to yield the title compound as a low melting red solid after column chromatography.

#### Example 64

##### 1-Oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxa-6-trimethylammoniumhexyloxy)piperidine Chloride

The title compound is prepared by reacting the glycidyloxy compound of Example 63 with choline chloride [(2-hydroxyethyl)trimethylammonium chloride].

#### Example 65

##### 1-Oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy- 3-trimethylammoniumpropoxy)piperidine Chloride

To 25 mL of 0.4 molar aqueous trimethylammonium hydroxide (0.01 mol) is added 2.28 g (0.01 mol) of 1-oxyl-2,2,6,6-tetramethyl-4-glycidyloxypiperidine. The mixture is stirred at ambient temperature for 16 hours. The solution is then neutralized with one equivalent of hydrochloric acid, washed twice with 50 mL of ethyl acetate and concentrated under reduced pressure. The resulting red oil is purified by column chromatography yielding 1.0 g of the title compound as a red oil.

#### Example 66

##### 1-Oxyl-2,2,6,6-tetramethyl-4-{2-hydroxy-3-[di(2-hydroxyethyl)amino]propoxy)piperidine

A solution of 2.28 g (0.01 mol) of 1-oxyl-2,2,6,6-tetramethyl-4-glycidyloxypiperidine and 1.05 g (0.01 mol) of diethanolamine in 25 mL of water is stirred at ambient temperature for 16 hours.

The solution is then extracted with methylene chloride. The methylene chloride extract is dried over anhydrous magnesium sulfate, filter and concentrated. The crude reaction product is purified by column chromatography to afford 1.0 g of the title compound as a red oil.

#### Example 67

##### 1-Oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-3-dimethylaminopropoxy)piperidine

A mixture of 10.0 g (0.044 mol) of 1-oxyl-2,2,6,6-tetramethyl-4-glycidyloxypiperidine and 10 mL of 40 % (ca. 0.091 mol) of dimethylamine (w/w) is dissolved in 100 mL of water and then stirred for 16 hours at ambient temperature. Water is then removed by vacuum distillation to leave 10 g of the title compound as a red oil.

#### Example 68

##### 1-Oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-3-diethylaminopropoxy)piperidine

The title compound is prepared according to the procedure of Example 67 when the dimethylamine is replaced with an equivalent amount of diethylamine. The product is purified by column chromatography and is isolated as a red oil.

#### Example 69

##### N,N'-Dimethyl-N,N'-bis-[3-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yloxy)-2-hydroxypropyl]hexamethylenediamine

The title compound is prepared according to the procedure of Example 4 replacing diethanolamine with an equivalent amount of N,N'-dimethylhexamethylenediamine. The product is purified by column chromatography and is isolated as a red oil.

#### Example 70

##### N,N,N',N'-Tetramethyl-N,N'-bis-[3-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yloxy)-2-hydroxypropyl]-hexamethylenediammonium Dibromide

A solution of 3.0 g (0.011 mol) of the compound of Example 67 and 0.89 g (0.0036 mol) of dibromohexane in 25 mL of absolute ethanol is refluxed for 16 hours. The resultant solution is concentrated under reduced pressure and the residue is washed thrice with 20 mL of ethyl acetate and then dried under vacuum. The title compound is obtained in a yield of 3.0 g as a red solid.

Example 71

1-Oxyl-2,2,6,6-tetramethyl-4-[2-hydroxy-3-(N,N-dimethyl-N-propylammonium)propoxy]piperidine Chloride

The title compound is prepared according to the procedure of Example 70 by replacing 1,6-dibromohexane with an equivalent amount of 1-bromopropane. The title compound is isolated as a red oil.

Example 72

Ethyl 1-Oxyl-2,2,6,6-tetramethyl-piperidin-4-yloxyacetate

To a solution of 3.0 g (17 mmol) of 1-oxyl-2,2,6,6-tetra methyl-4-hydroxypiperidine in 25 mL of anhydrous tetrahydrofuran is added 0.48 g (20 mmol) of sodium hydride. The reaction mixture is stirred under a blanket of nitrogen for one hour. The mixture is then chilled to 0°C and 2.9 g (17 mmol) of ethyl bromoacetate is added dropwise. After the addition, the reaction mixture is stirred for an additional 30 minutes during which time a precipitate forms. The mixture is filtered and the solvent is removed under reduced pressure. The title compound is isolated after column chromatography as an orange solid melting at 41-43°C.

Example 73

1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yloxyacetic Acid

To a solution of 0.2 g of sodium hydroxide in 20 mL of 1:1 water:methanol is added 1.0 g (39 mmol) of the compound of Example 72. The mixture is stirred for one hour and then carefully acidified with 1% aqueous hydrochloric acid. The resultant mixture is extracted with ethyl acetate. The organic extract is dried over anhydrous magnesium sulfate and concentrated under reduced pressure to afford the title compound as an orange solid.

Example 74

Sodium 1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yloxyacetate

To a solution of 1.0 g (4.3 mmol) of the compound of Example 73 dissolved in 20 mL of water is added 0.17 g (4.3 mmol) of sodium hydroxide. The solution is stirred for one hour and the water is then removed by vacuum distillation to afford the title compound as an orange solid.

Example 75

## 1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yloxyacetic Acid Choline Ester

The title compound is prepared by reacting the acid of Example 73 with choline chloride [(2-hydroxyethyl)trimethylammonium chloride].

Example 76

## 1-Hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium Chloride

67 mL of isopropanol is cooled to 0°C and saturated with HCl gas. This solution is added dropwise to a mechanically stirred solution of 50 g (0.29 mol) 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine in 130 mL of isopropanol, maintaining a reaction temperature of about 20°C by occasionally cooling with an ice bath. The HCl salt is vacuum filtered and washed with isopropanol, giving a pale yellow solid. 5.0 g of this crude product is recrystallized from 100 mL isopropanol affording 3 g of a white crystalline solid, mp >260°C.

Elemental Analysis:

	<u>Calc.</u>	<u>Found</u>
%C	51.55	51.30
%H	9.61	9.70
%N	6.68	6.42
%Cl	16.91	16.83

Example 77

## 1-Hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium Acetate

5.0 g (0.029 mol) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidine and 2.0 g (0.033 mol) acetic acid are recrystallized from 50 mL of isopropanol, yielding 4.0 g of the desired hydroxylamine salt as a white crystalline solid, mp 140-143°C.

Elemental Analysis:

	<u>Calc.</u>	<u>Found</u>
%C	56.63	56.78
%H	9.94	10.13
%N	6.00	6.07



Example 78

## 1-Hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium Bisulfate

5.0 g (0.029 mol) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidine and 3.0 g (0.031 mol) sulfuric acid are recrystallized from 50 mL of isopropanol, yielding 3.0 g of the desired hydroxylamine salt as a white crystalline solid, mp 238-241°C.

Elemental Analysis:

	<u>Calc.</u>	<u>Found</u>
%C	39.99	40.06
%H	7.46	8.06
%N	5.18	5.11
%S	11.86	11.87

Example 79

## 1-Hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium Bisulfate

2.6 ml of concentrated sulfuric acid is added dropwise to a solution of 10.0g (46.9 mmol) 1-oxyl-2,2,6,6-tetramethyl-4-acetamidopiperidine in 50 ml isopropanol. After 48 hrs the resulting white solid is collected by filtration, washed with isopropanol and dried under vacuum, mp 198°C.

Elemental Analysis:

	<u>Calc.</u>	<u>Found</u>
%C	42.28	42.23
%H	7.76	7.76
%N	8.97	8.85

Example 80

## Bis-(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) Oxalate

To a glass 0.5L reaction bottle are added 10.0 g (58 mmol) of C, 5.22 g (58 mmol) oxalic acid, 200 mg 5% Pt on C and 100 mL water. Catalytic hydrogenation is carried out at 50 psi for 30 minutes at room temperature. Catalyst is removed by vacuum filtration with Celite. Water is removed by distillation under reduced pressure, giving a colorless solid. The crude product is

recrystallized from 100 mL isopropanol affording 3.5 g of the product as a white crystalline solid, mp 244°C.

Elemental Analysis:

	<u>Calc.</u>	<u>Found</u>
%C	55.03	54.69
%H	9.24	9.49
%N	6.42	6.32

#### Example 81

Tris-(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) Citrate

To a glass 0.5L reaction bottle are added 20.0 g (116 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, 7.39 g (38.5 mmol) citric acid, 200 mg 5% Pt on C and 100 mL water. Catalytic hydrogenation is carried out at 50 psi for 30 minutes at room temperature. Catalyst is removed by filtration through a pad of Celite. The aqueous salt solution has a pH of 5.56. Removal of water yields the product as a hygroscopic glassy solid.

#### Example 82

Bis-(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) Citrate

To a glass 0.5L reaction bottle are added 20.0 g (116 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, 11.12 g (58 mmol) citric acid, 200 mg 5% Pt on C and 100 mL water. Catalytic hydrogenation is carried out at 50 psi for 30 minutes at room temperature. Catalyst is removed by filtration through a pad of Celite. The aqueous salt solution has a pH of 4.39. Removal of water yields the product as a hygroscopic glassy solid.

#### Example 83

1-Hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium Citrate

To a glass 0.5L reaction bottle are added 20.0 g (116 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, 22.2 g (116 mmol) citric acid, 200 mg 5% Pt on C and 100 mL water. Catalytic hydrogenation is carried out at 50 psi for 30 minutes at room temperature. Catalyst is removed by filtration through a pad of Celite. The aqueous salt solution has a pH of 3.30. Removal of water yields the product as a hygroscopic glassy solid.

Example 84

## Bis-(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) Sulfate

To a glass 0.5L reaction bottle are added 10.0 g (58 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, 2.85g (29 mmol) sulfuric acid, 200 mg 5% Pt on C and 100 mL water. Catalytic hydrogenation is carried out at 50 psi for 30 minutes at room temperature. Catalyst is removed by filtration through a pad of Celite.. Removal of water yields the product as a pale yellow solid.

The following examples are compounds of the formulae III-IIIe.

Example 85

## 1-Oxyl-2,2,6,6-tetramethyl-4-allyloxypiperidine

A vigorously stirred two phase solution of 30.0 g (0.17 mol) 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, 29.0 g (0.24 mol) of allyl bromide, 2.6 g (8 mmol) of tetrabutylammonium bromide, 100 mL of 50% aqueous sodium hydroxide and 30 mL of toluene is heated at 70°C for 90 minutes. The mixture is partitioned between 100 mL of toluene, 100 mL of heptane and 200 mL of water. The organic phase is dried over anhydrous magnesium sulfate and concentrated to yield the title compound as a red oil after column chromatography.

Example 86

## 1-Oxyl-2,2,6,6-tetramethyl-4-(2-methoxyethoxy)piperidine

The title compound is synthesized using the same procedure as described in Example 85 and using 2-bromoethyl methyl ether in place of allyl bromide. The product is isolated as a red oil after column chromatography.

Example 87

## 1-Oxyl-2,2,6,6-tetramethyl-4-glycidyloxypiperidine

The title compound is synthesized using the same general procedure as described in Example 85 and using epichlorohydrin in place of allyl bromide. The product is isolated as a low melting red solid after column chromatography.

Example 88

## 1-Oxyl-2,2,6,6-tetramethyl-4-(2,3-dihydroxypropoxy)piperidine

1.0 g of the compound of Example 87 is heated at 110 °C in 50 mL of 5% aqueous sodium hydroxide for six hours. The mixture is extracted with ethyl acetate, and the organic extract is dried and concentrated. The title compound is isolated as a red oil after column chromatography.

Example 89

## 1-Oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine

1.0 g of the compound of Example 87 is heated at 60 °C in a solution of 0.25 g sodium methoxide in 50 mL of methanol for six hours. The reaction mixture is then partitioned between water and ethyl acetate. The title compound is isolated as a red oil after column chromatography.

Example 90

## 1-Oxyl-2,2,6,6-tetramethyl-4-(carboethoxymethoxy)piperidine

0.48 g (20 mmol) of sodium hydride is added to a solution of 3.0 g (17 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine in 25 mL of anhydrous tetrahydrofuran. The reaction mixture is stirred under a blanket of nitrogen for one hour. The mixture is chilled to 0 °C and 2.9 g (17 mmol) of ethyl bromoacetate is added dropwise. After the addition is complete, the reaction is stirred for an additional 30 minutes during which time a white precipitate forms. The mixture is filtered and the solvent is removed under reduced pressure. The title compound is isolated as an orange solid after column chromatography and melts at 41-43 °C.

Example 91

## 1-Oxyl-2,2,6,6-tetramethyl-4-(carboxymethoxy)piperidine

1.0 g (39 mmol) of the compound of Example 90 is added to a solution of 0.2 g sodium hydroxide in 20 mL of 1:1 water/methanol. The mixture is stirred for one hour, carefully acidified with 1% aqueous hydrogen chloride and then extracted with ethyl acetate. The organic extract is dried over anhydrous magnesium sulfate and then concentrated to afford the title compound as an orange solid.

Example 92

## 1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl-2-Methoxyethoxyacetate

34.4 grams of 1-oxy-2,2,6,6-tetramethyl-4-hydroxypiperidine, 29.6 grams of methyl 2-methoxyethoxyacetate and 300 mL of heptane are transferred to a 500 mL 3-necked, round-bottomed flask equipped with a mechanical stirrer, Dean-Stark trap and condenser. Trace amounts of water are removed by azeotropic distillation. 0.25 mL of tetraisopropyl orthotitanate is added to the reaction mixture. The reaction mixture is refluxed for six hours and the liberated methanol is collected in the Dean-Stark trap. The reaction mixture is allowed to cool and is then partitioned between 300 mL of ethyl acetate and 300 mL of water. The phases are separated and the organic phase is washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent leaves the title compound as a red oil.

#### Example 93

##### 1-Oxy-2,2,6,6-tetramethylpiperidin-4-yl 2-(2-Methoxyethoxy)ethoxyacetate

The title compound is synthesized using the same procedure as described in Example 92 and using methyl 2-(2-methoxyethoxy)ethoxyacetate in place of methyl 2-methoxyethoxyacetate. The title compound is isolated as a red oil after column chromatography.

#### Example 94

##### 1-Oxy-2,2,6,6-tetramethylpiperidin-4-yl Methoxyacetate

The title compound is synthesized using the same procedure as described in Example 92 and using methyl methoxyacetate in place of methyl 2-methoxyethoxyacetate. The title compound is isolated as an orange solid by crystallization from heptane and melts at 103°C.

#### Example 95

##### 1-Oxy-2,2,6,6-tetramethylpiperidin-4-yl Methyl Succinate

A solution of 6.0 g (35 mmol) of 1-oxy-2,2,6,6-tetramethyl-4-hydroxypiperidine and 11.4 g (78 mmol) dimethyl succinate in 60 mL of heptane is brought to reflux. 0.05 mL of tetraisopropyl orthotitanate is added and the reaction mixture is refluxed for 16 hours while the evolved methanol is trapped in a Dean-Stark trap. The reaction mixture is then concentrated and the title compound is isolated as a red oil after column chromatography and melts at 76°C.

#### Example 96

##### 1-Oxy-2,2,6,6-tetramethylpiperidin-4-yl Acetoacetate

The title compound is synthesized using the same procedure as described in Example 95 but using methyl acetoacetate in place of dimethyl succinate. The title compound is isolated as a

red oil after column chromatography.

#### Example 97

##### 1-Oxyl-2,2,6,6-tetramethyl-piperidin-4-yl Butylcarbamate

0.1 g of di-n-butyltin dilaurate is added to a solution of 1.0 g (5.8 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and 0.58 g (5.8 mmol) of butyl isocyanate in 10 mL of carbon tetrachloride. After stirring for four hours at ambient temperature, the solution is concentrated and the title compound is isolated as a red oil after column chromatography.

#### Example 98

##### N-(1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide

The title compound is prepared according to the procedure of E. J. Vlietstra et al., *Macromolecules*, 1990, 23, 946.

#### Example 99

##### N-(1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl)octanamide

To a stirred 0 °C solution of 1.0 g of 1-oxyl-4-amino-2,2,6,6-tetramethylpiperidine and 0.65 g of triethylamine in 10 mL of methylene chloride is added dropwise a solution of 0.95 g of octanoyl chloride in 5 mL of methylene chloride. After the addition is complete, the reaction mixture is allowed to warm to ambient temperature. After two more hours, the reaction mixture is washed with 1% aqueous sodium hydroxide and finally water. The organic phase is dried over anhydrous magnesium sulfate, filtered and concentrated. The title compound is isolated as a red oil after column chromatography.

#### Example 100

##### N-(1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl)methoxyacetamide

The title compound is synthesized using the same general procedure as described in Example 99 and using methoxyacetyl chloride in place of octanoyl chloride. The title compound is isolated as an orange solid after column chromatography and melts at 124-125 °C.

#### Example 101

##### N-(1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-2-methoxyethoxyacetamide

The title compound is synthesized using the same general procedure as described in Example 99 and using methoxyethoxyacetyl chloride in place of octanoyl chloride. The title compound is

isolated as a red oil after column chromatography.

#### Example 102

##### 1-Butyl-3-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)urea

To a stirred solution of 1.0 g of 1-oxyl-4-amino-2,2,6,6-tetramethylpiperidine in 75 mL of dry toluene is added dropwise 0.65 mL of butyl isocyanate. The reaction mixture is stirred for 16 hours. The solution is then concentrated to yield the title compound as a red oil.

#### Example 103

##### N-Butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide

A pressure reactor is charged with 10 g of 4-butylamino-2,2,6,6-piperidine and 100 mL of ethyl formate and then purged with nitrogen. The reactor is immersed in an 100 °C oil bath for three hours. A maximum pressure of 24 psi is observed. The resultant ethanol and unreacted ethyl formate are distilled off under vacuum.

The intermediate N-formyl amine product is then oxidized to corresponding nitroxide as seen below.

To a refluxing solution of the 20 g of the intermediate N-formyl amine and 0.3 g of molybdenum trioxide in 200 mL of methylene chloride is added 60 mL of 70% aqueous tert-butyl hydroperoxide in 10 mL portions over a six hour period. The molybdenum catalyst is then removed by filtration. The filtrate is washed with water, dried over anhydrous magnesium sulfate, filtered and concentrated to yield the title compound as an orange solid which melts at 77-79 °C.

#### Example 104

##### N-Butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)acetamide

To a stirred solution of 95 g of 4-butylamino-2,2,6,6-tetramethylpiperidine in 500 mL of diethyl ether is added dropwise 50 mL of acetic anhydride. After the addition is complete, the reaction mixture is stirred at 0 °C for one hour and then at 20 °C for three hours. The resulting precipitate is collected by filtration and washed with diethyl ether till all the orange color is removed. The free amine intermediate is isolated by partitioning the solid between aqueous sodium hydroxide and ether.

The intermediate N-acetyl amine product is then oxidized to the corresponding nitroxide as follows:

To a stirred 50 °C solution of 13.3 g of N-butyl-N-(2,2,6,6-tetramethylpiperidin-4-yl)acetamide, 0.075 g of sodium tungstate-dihydrate and 0.075 g of ethylenediaminetetraacetic acid in 25 mL of methanol is added 35 mL of 30% aqueous hydrogen peroxide over a three hour period. After the addition is complete, the reaction mixture is stirred another two hours. The reaction mixture is then partitioned between diethyl ether and water. The organic phase is washed with water, 1% aqueous hydrogen chloride and then water. After drying over anhydrous magnesium sulfate and concentrating, the title compound is obtained as a red solid. After crystallization from hexane, the compound melts at 84-85 °C.

#### Example 105

N-(1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl)caprolactam

This compound is prepared by the method of Example 14 of United States Patent No. 4,472,547.

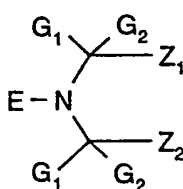


## WHAT IS CLAIMED IS:

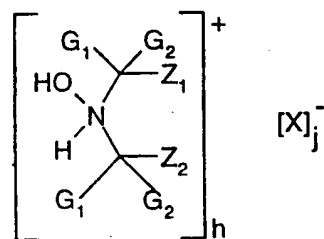
1. A composition having reduced loss of brightness and enhanced resistance to yellowing which comprises

(a) a pulp or paper which still contains lignin, and

(b) and effective stabilizing amount of a hindered amine compound of formula I or II



(I)



(II)

where

$G_1$  and  $G_2$  are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene,

$Z_1$  and  $Z_2$  are each methyl, or  $Z_1$  and  $Z_2$  together form a linking moiety which may additionally be substituted by an ester, ether, hydroxy, oxo, cyanohydrin, amide, amino, carboxy or urethane group,

$E$  is oxyl, hydroxyl, hydrogen, alkyl, alkyl substituted by hydroxyl, oxo or carboxy or interrupted by oxygen or carboxy alkenyl, alkynyl, cycloalkyl, cycloalkenyl, bicycloalkyl, alkoxy, alkoxy substituted by hydroxyl, oxo or carboxy or interrupted by oxygen or carboxy, cycloalkoxy, alkenyloxy, cycloalkenyloxy, aralkyl, aralkoxy, acyl,  $R'(C=O)O-$ ,  $R'O(C=O)O-$ ,  $R'N(C=O)O-$  or chloro, where  $R'$  is an aliphatic or aromatic moiety,

$X$  is an inorganic or organic anion, and

where the total charge of cations  $h$  is equal to the total charge of anions  $j$ , and with the proviso that the compound of formula I is not bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate or the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid.

2. A composition according to claim 1 where in the compound of component (b), E is oxyl, hydroxyl, hydrogen, alkyl of 1 to 18 carbon atoms, alkyl of 2 to 12 carbon atoms substituted by one to three hydroxyl or said alkyl interrupted by one to four oxygen atoms, or said alkyl both substituted by said hydroxyl groups and interrupted by said oxygen atoms, alkenyl of 2 to 18 carbon atoms, alkynyl of 2 to 12 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, cycloalkenyl of 5 to 12 carbon atoms, bicycloalkyl of 6 to 10 carbon atoms, alkoxy of 1 to 18 carbon atoms, alkoxy of 2 to 12 carbon atoms substituted by one to three hydroxyl groups or said alkoxy interrupted by one to four oxygen atoms or said alkoxy substituted by -COOZ where Z is hydrogen or alkyl of 1 to 4 carbon atoms, cycloalkoxy of 5 to 12 carbon atoms, cycloalkenyloxy of 5 to 12 carbon atoms, alkenyloxy of 2 to 18 carbon atoms, aralkyl of 7 to 15 carbon atoms, aralkoxy of 7 to 15 carbon atoms, alkanoyl of 2 to 12 carbon atoms, alkenoyl of 3 to 12 carbon atoms, benzoyl, or  $R'(C=O)O-$ ,  $R'O(C=O)O-$ ,  $R'N(C=O)O-$ , where  $R'$  is alkyl of 1 to 6 carbon atoms or phenyl.

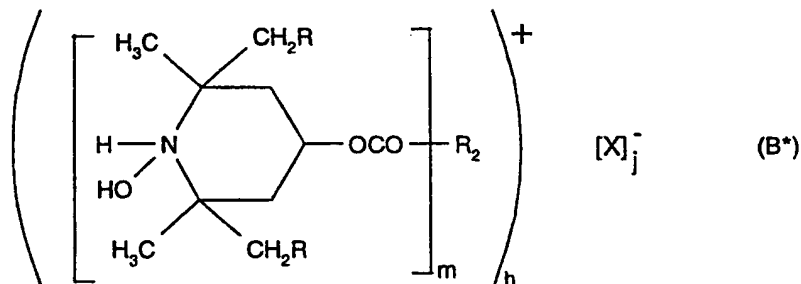
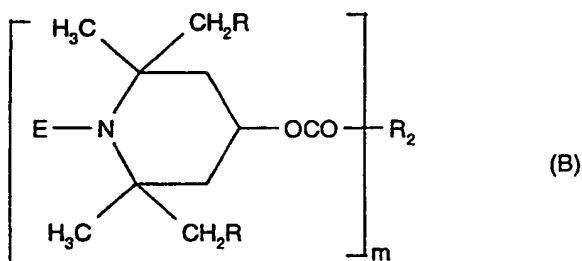
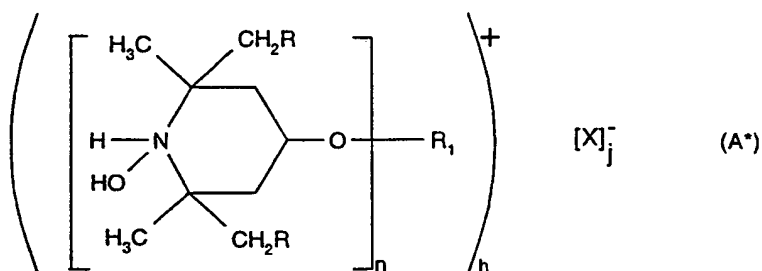
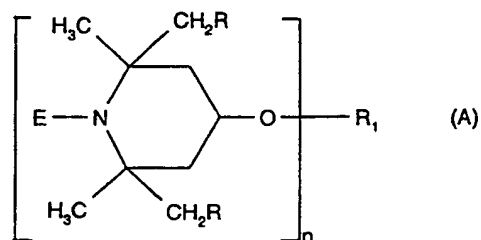
3. A composition according to claim 1 where in the compound of component (b), X is phosphate, carbonate, bicarbonate, nitrate, chloride, bromide, bisulfite, sulfite, bisulfate, sulfate, borate, carboxylate, an alkylsulfonate or an arylsulfonate, or a phosphonate.

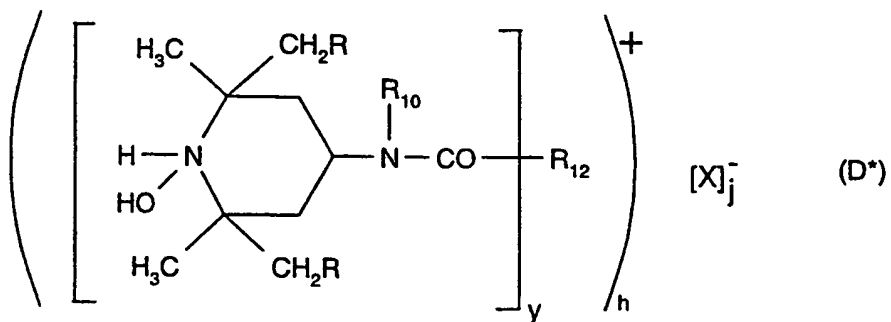
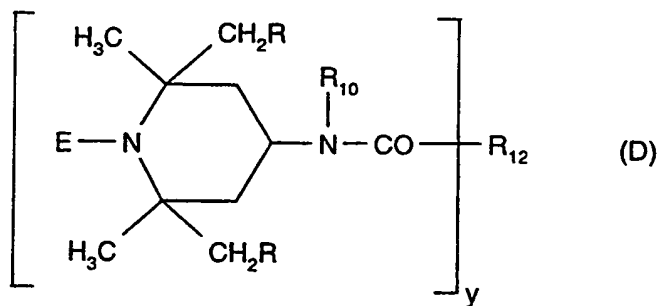
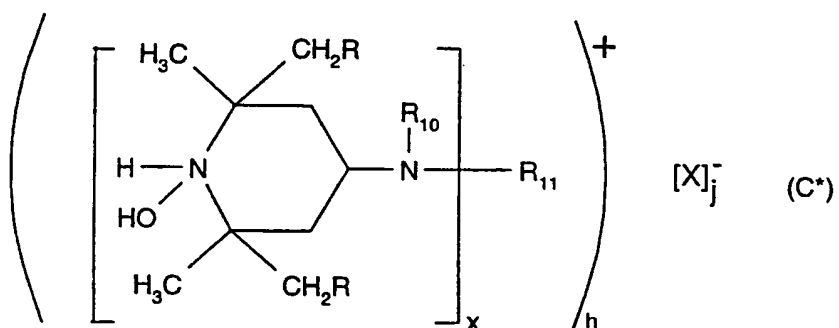
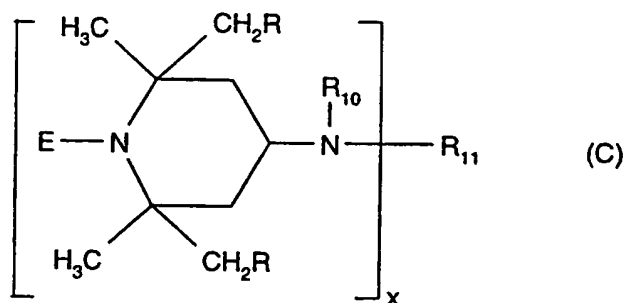
4. A composition according to claim 1 where in the compound of component (b), E is oxyl, hydroxyl, alkenyloxy of 2 to 18 carbon atoms, aralkoxy of 7 to 15 carbon atoms, alkoxy of 1 to 18 carbon atoms, or alkoxy of 2 to 12 carbon atoms substituted by oxo or interrupted by carboxy; and X is phosphate; carbonate; bicarbonate; nitrate; chloride; bromide; bisulfite; sulfite; bisulfate; sulfate; borate; a carboxylate of a mono-, di-, tri- or tetracarboxylic acid; an alkylsulfonate of 1 to 18 carbon atoms or an arylsulfonate of 6 to 12 carbon atoms, or a phosphonate.

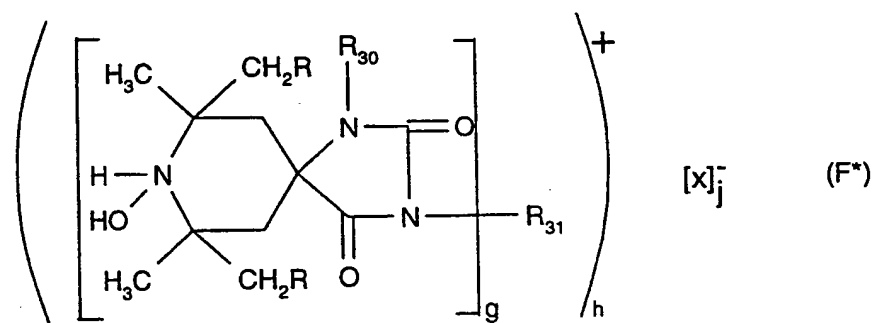
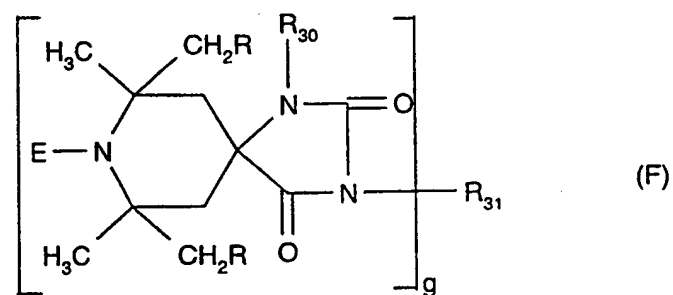
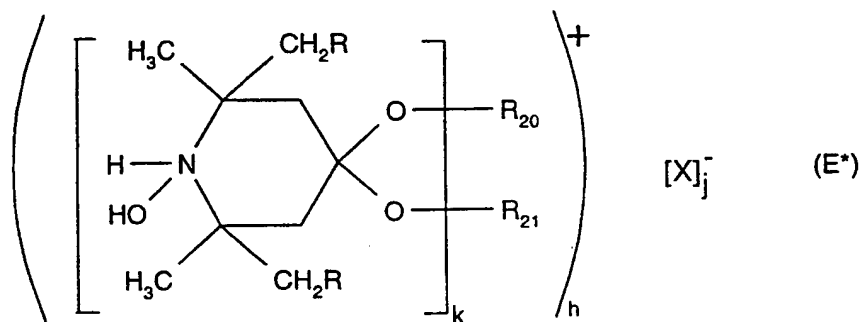
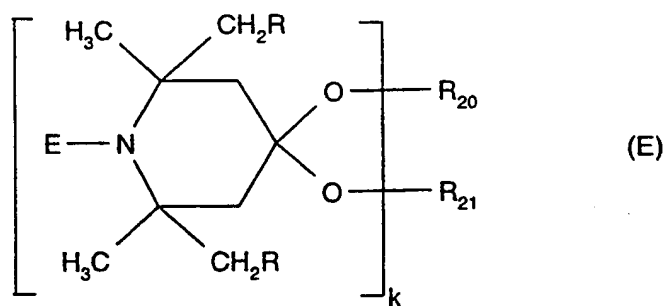
5. A composition according to claim 1 where in the compound of component (b), E is oxyl or hydroxyl; and  $Z_1$  and  $Z_2$  are each methyl or together are a hydrocarbon linking moiety

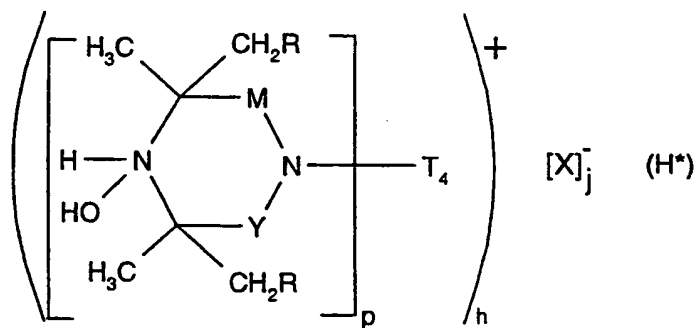
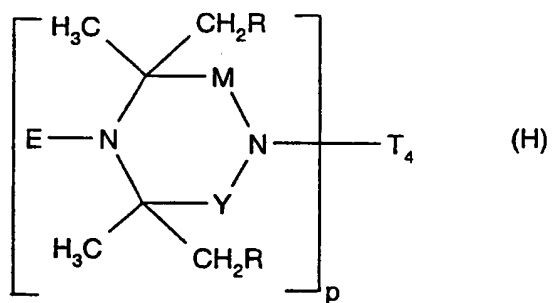
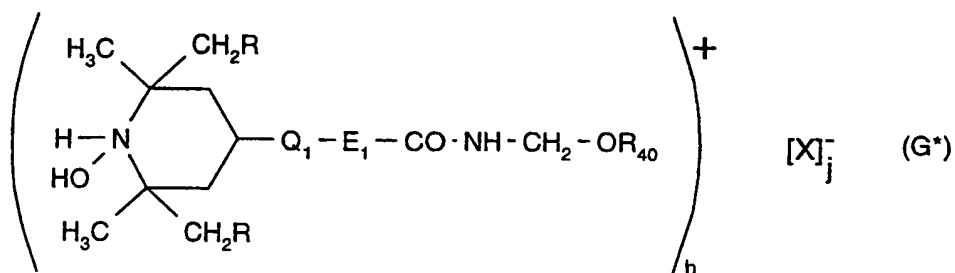
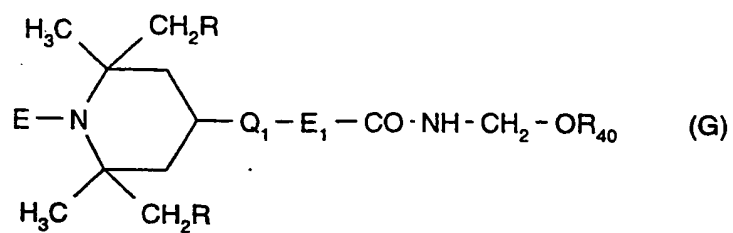
containing 1-200 carbon atoms and 0-60 heteroatoms selected from oxygen atoms and nitrogen atoms.

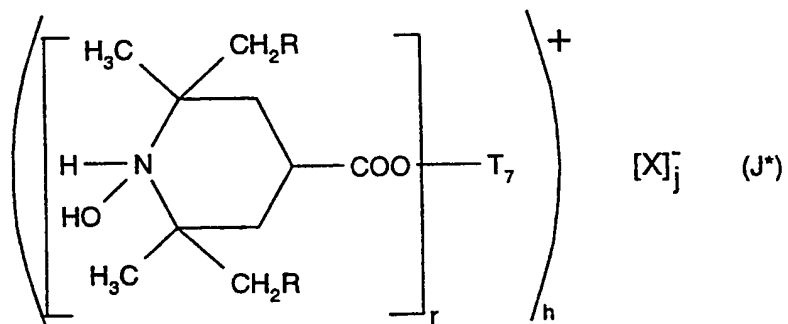
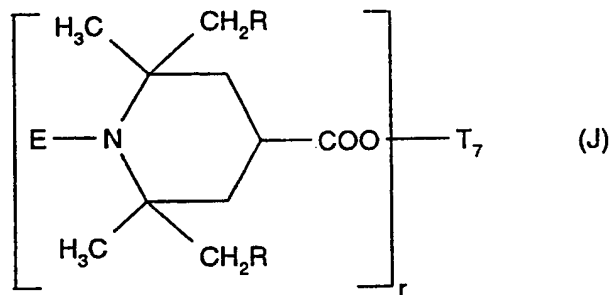
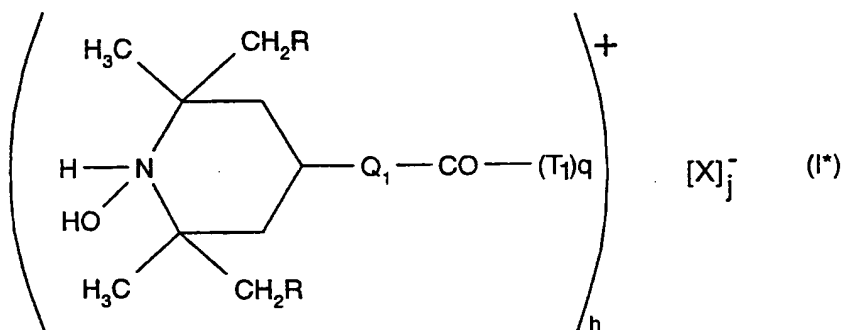
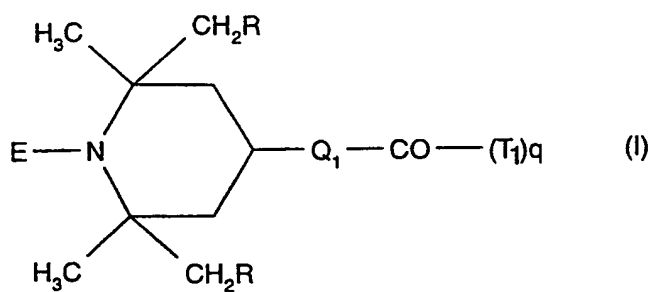
6. A composition according to claim 1 wherein the hindered amine compound of component (b) is selected from the compounds of formulas A to EE and A\* to EE\* and III to IIIc.

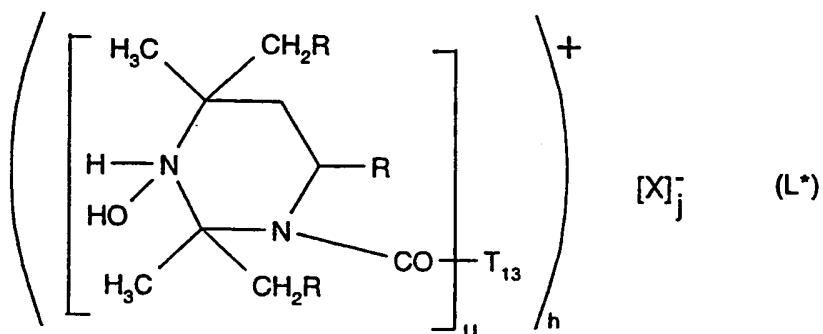
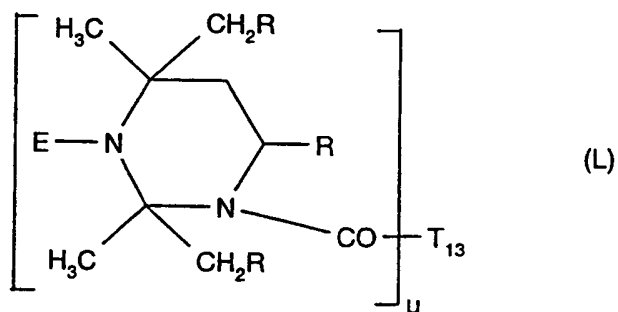
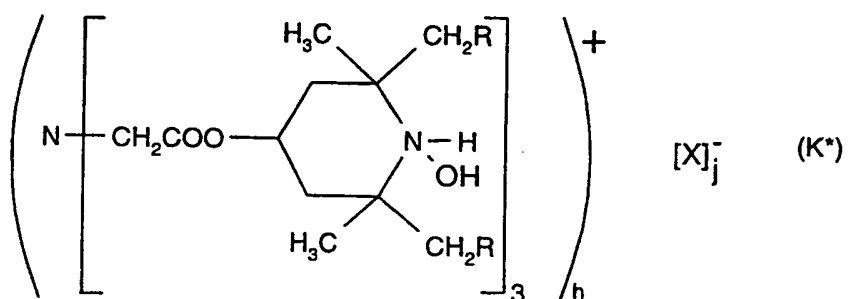
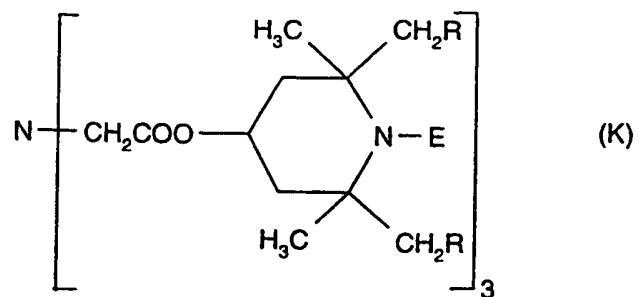




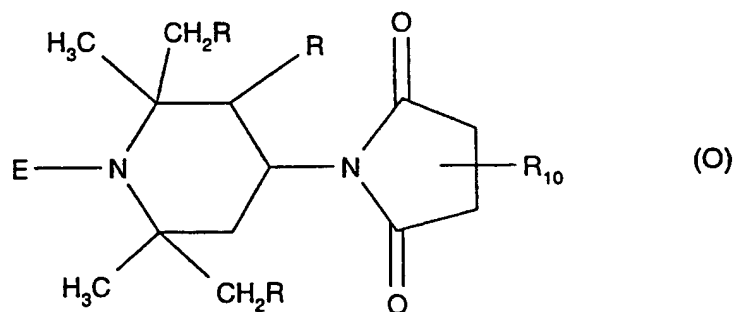
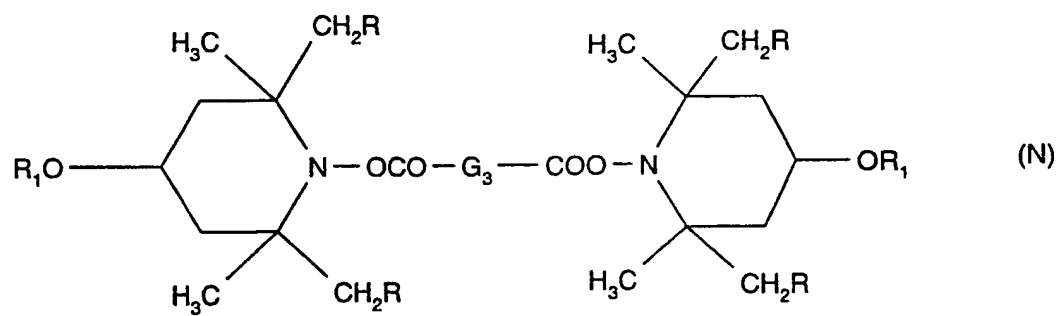
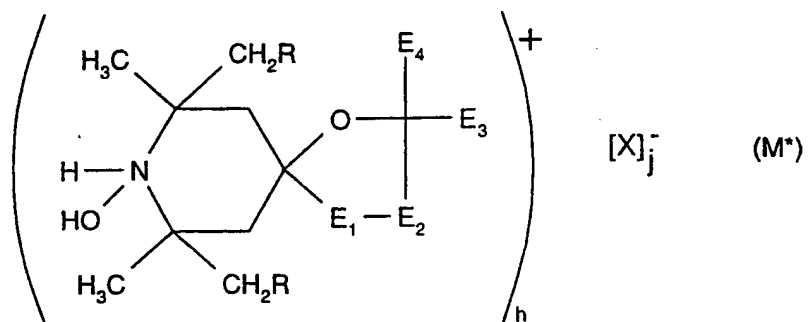
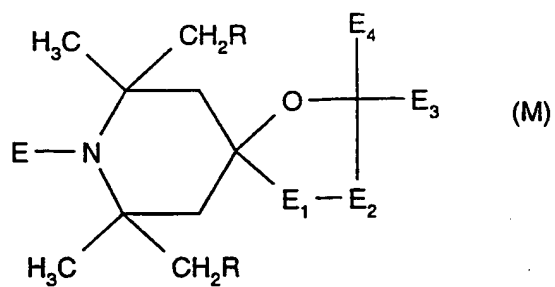


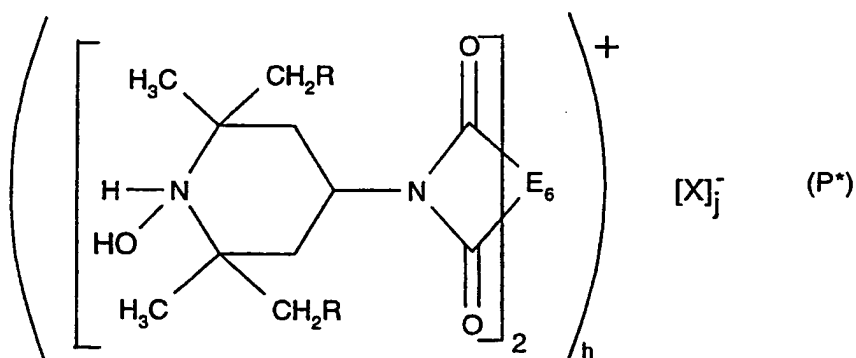
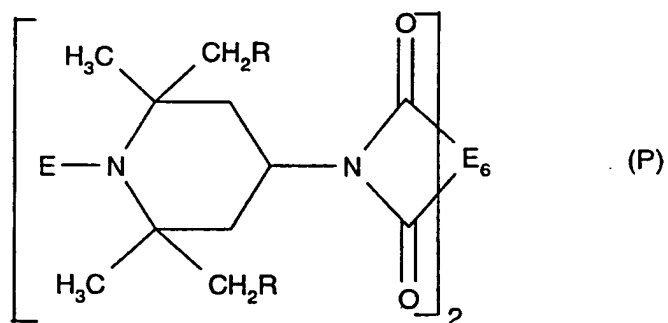
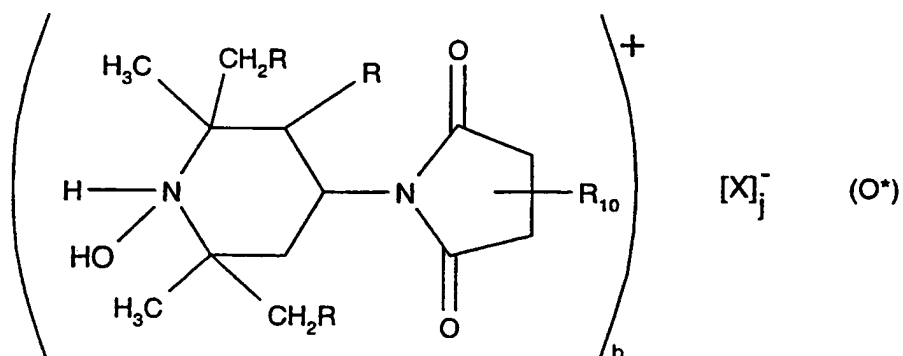


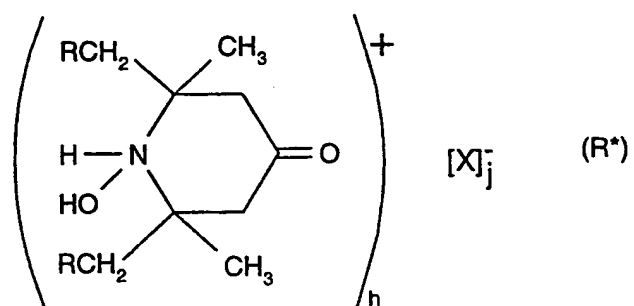
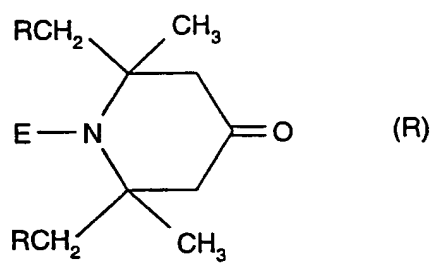
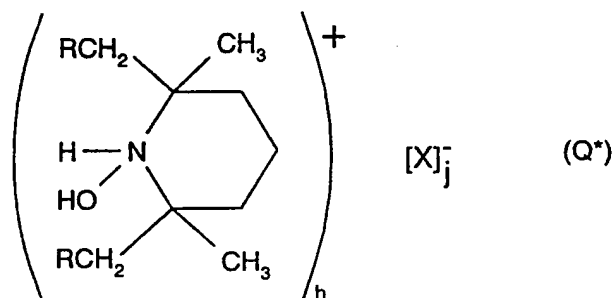
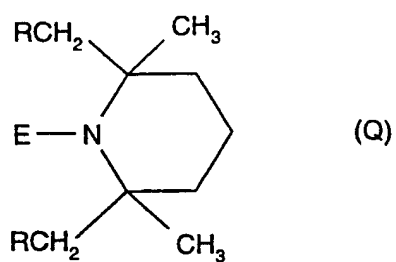


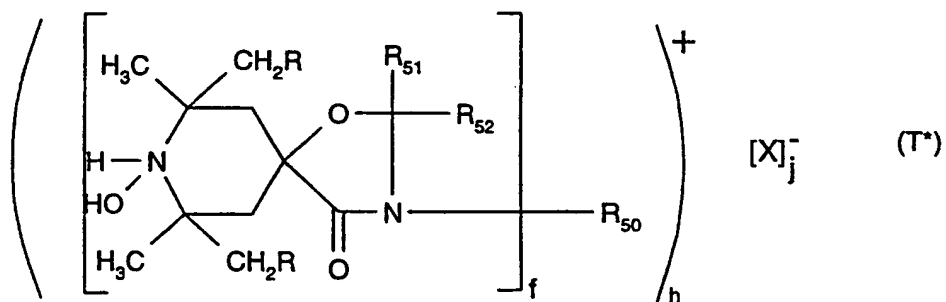
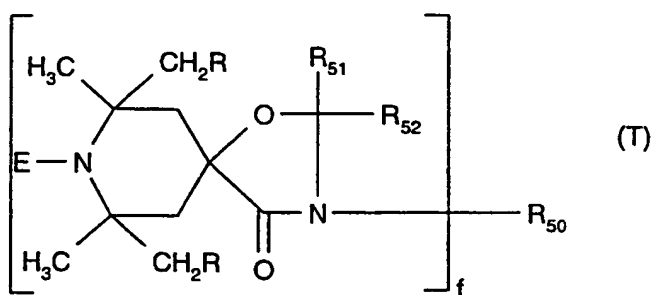
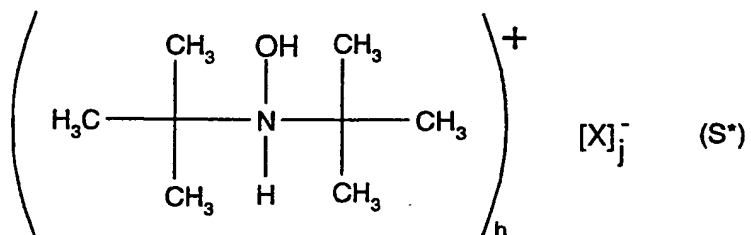
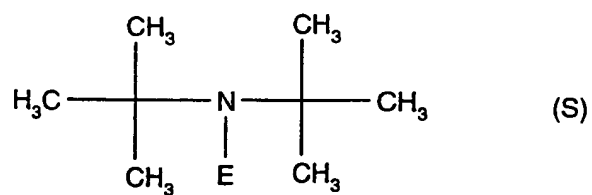


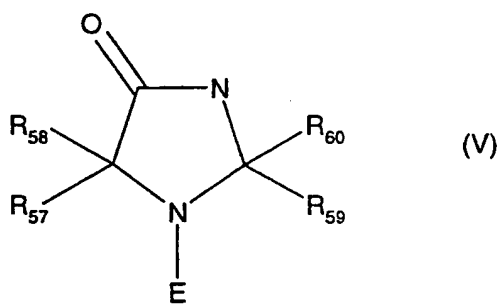
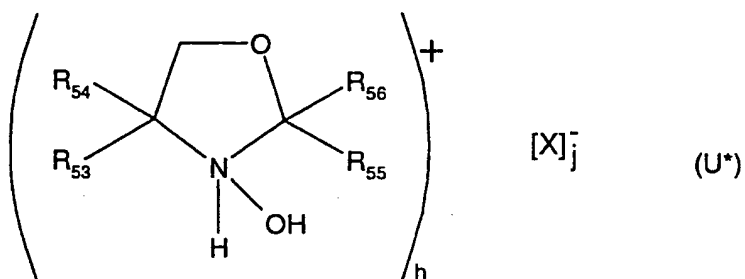
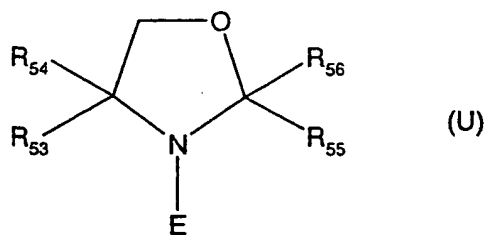


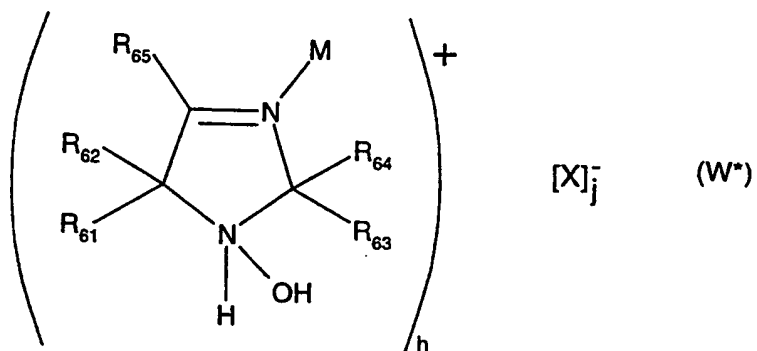
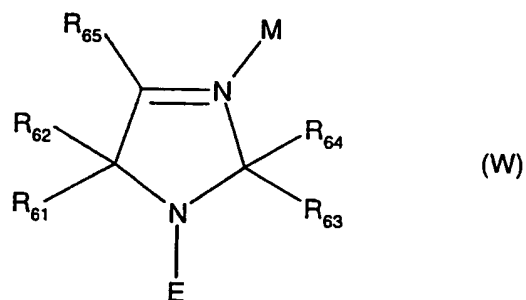
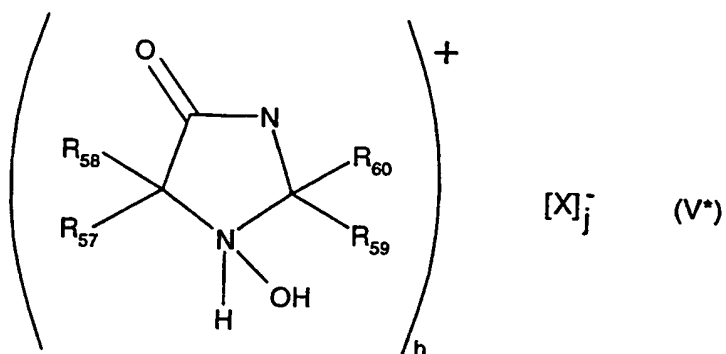


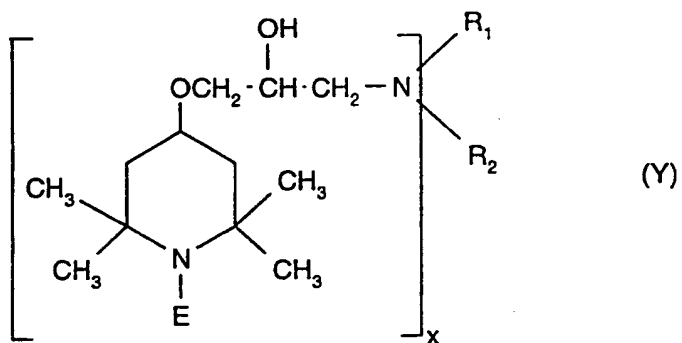
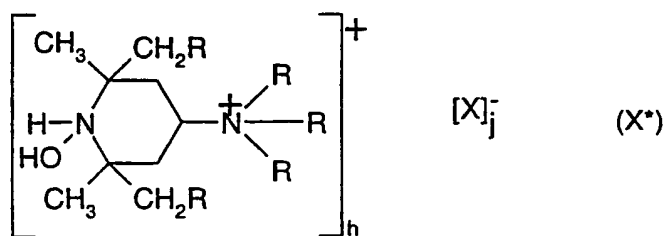
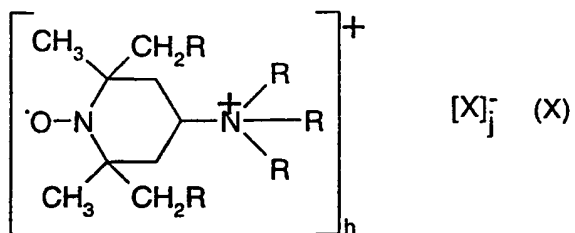


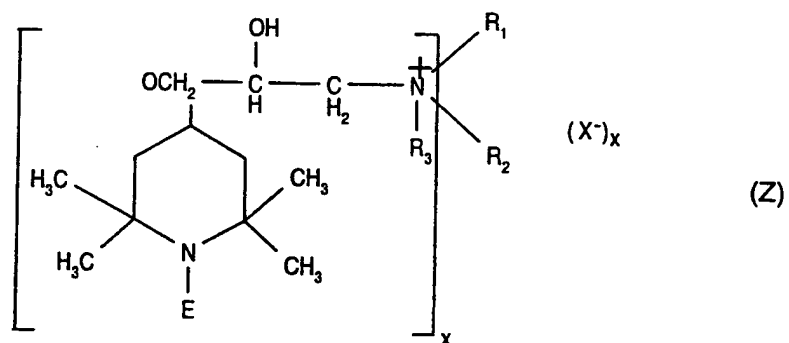
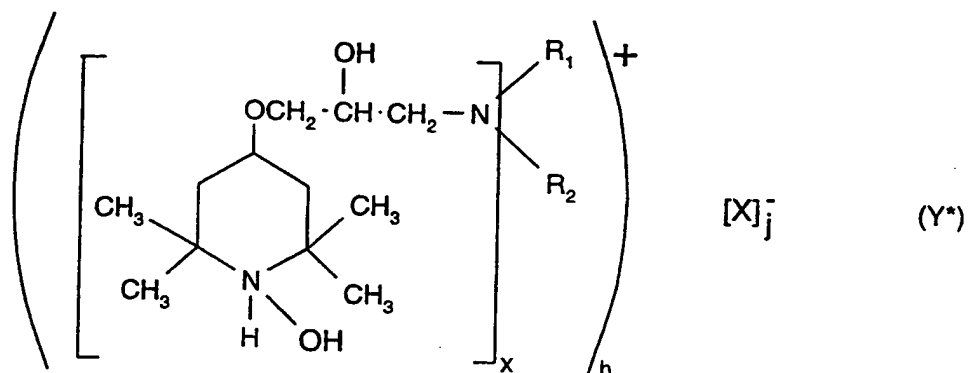




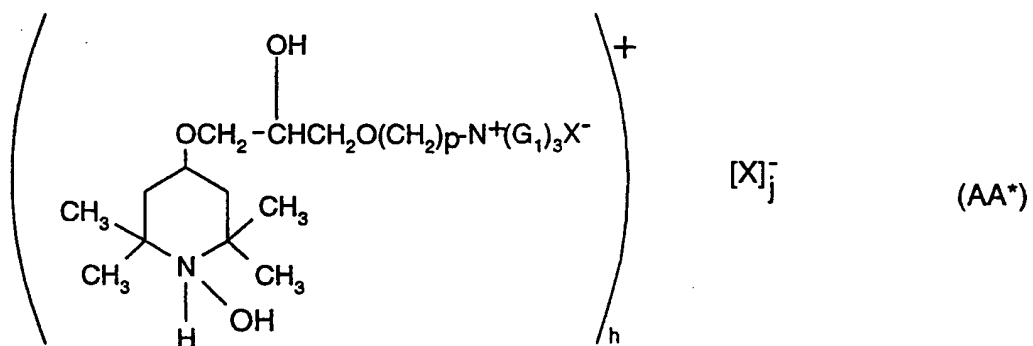
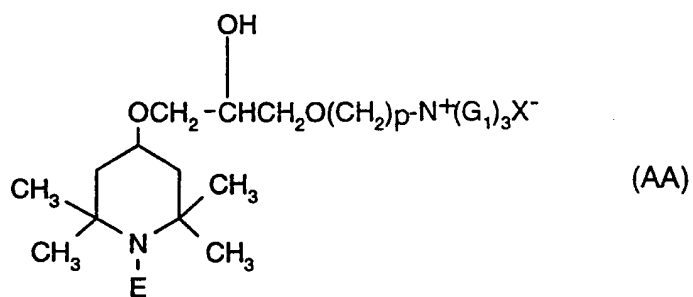
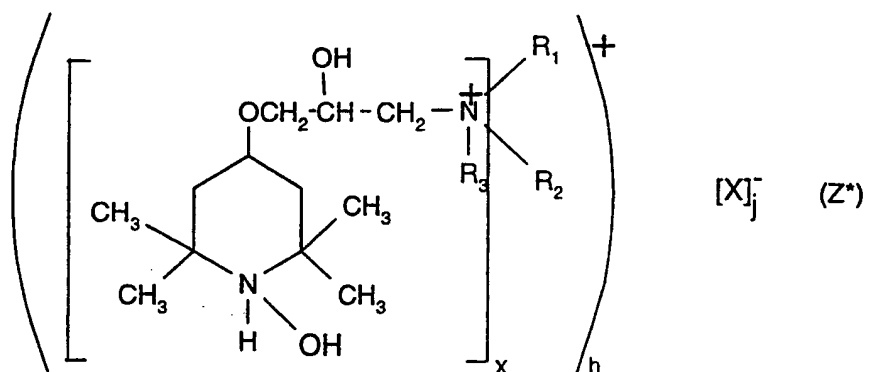


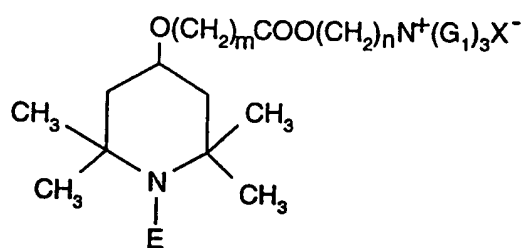




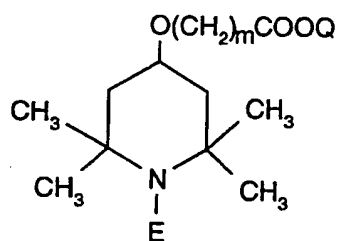
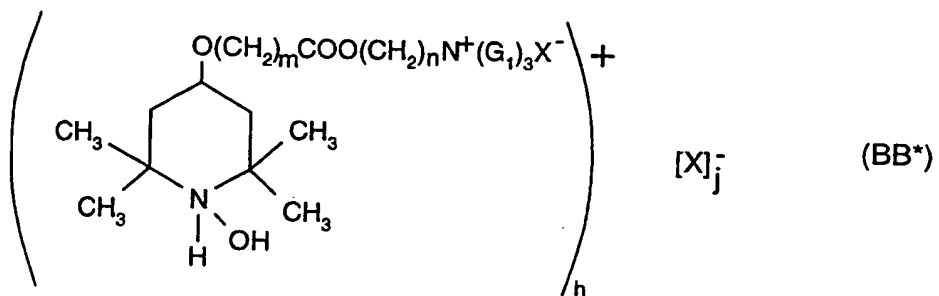




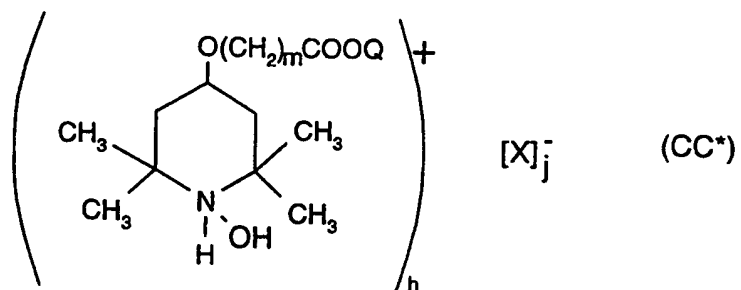


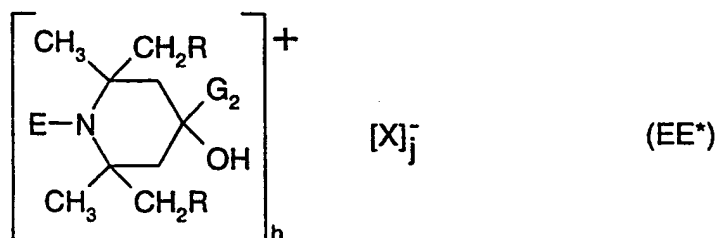
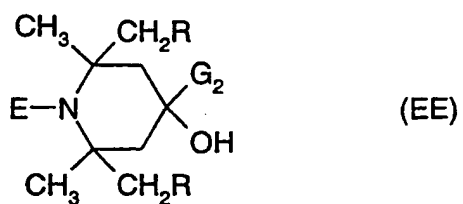
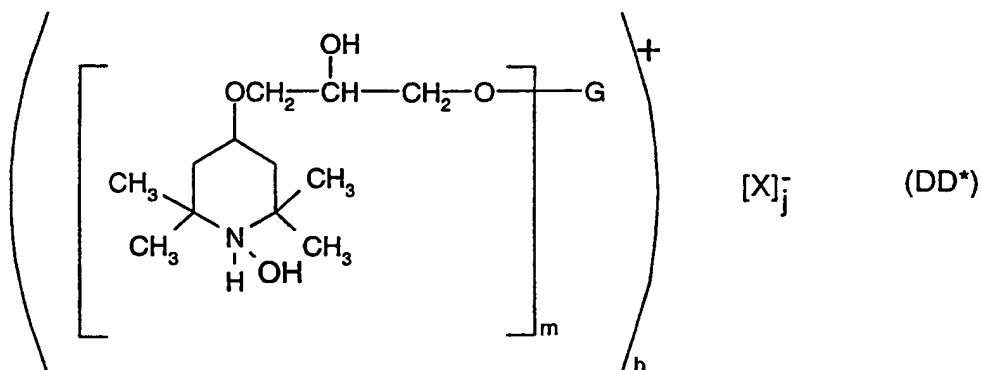
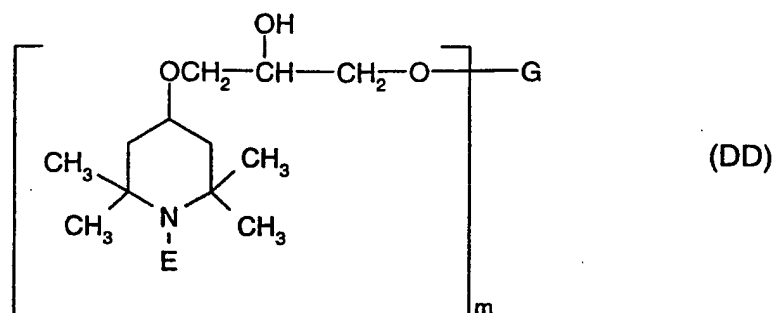


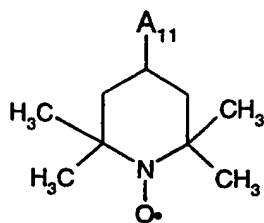
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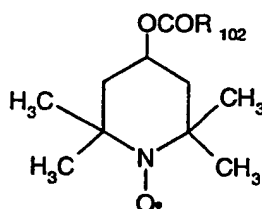
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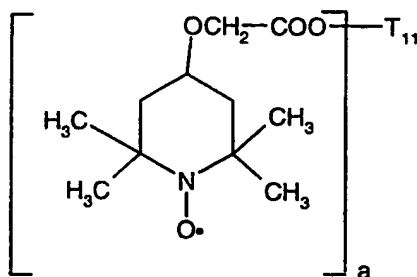




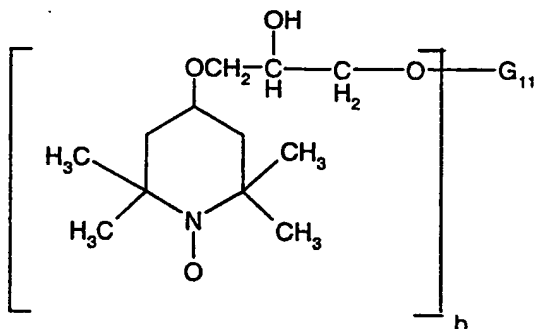
(III),



(IIIa),



(IIIb),



(IIIc)

wherein

E is oxyl, hydroxyl, hydrogen, alkyl of 1 to 18 carbon atoms, alkyl of 2 to 12 carbon atoms substituted by one to three hydroxyl or said alkyl interrupted by one to four oxygen atoms, or said alkyl both substituted by said hydroxyl groups and interrupted by said oxygen atoms, alkenyl of 2 to 18 carbon atoms, alkynyl of 2 to 12 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, cycloalkenyl of 5 to 12 carbon atoms, bicycloalkyl of 6 to 10 carbon atoms, alkoxy of 1 to 18 carbon atoms, alkoxy of 2 to 12 carbon atoms substituted by one to three hydroxyl groups or

said alkoxy interrupted by one to four oxygen atoms or said alkoxy substituted by -COOZ where Z is hydrogen or alkyl of 1 to 4 carbon atoms, cycloalkoxy of 5 to 12 carbon atoms, cycloalkenyloxy of 5 to 12 carbon atoms, alkenyloxy of 2 to 18 carbon atoms, aralkyl of 7 to 15 carbon atoms, aralkoxy of 7 to 15 carbon atoms, alkanoyl of 2 to 12 carbon atoms, alkenoyl of 3 to 12 carbon atoms, benzoyl, or  $R'(C=O)O-$ ,  $R'O(C=O)O-$ ,  $R'N(C=O)O-$ , where  $R'$  is alkyl of 1 to 6 carbon atoms or phenyl,

R is hydrogen or methyl,

in formula A and A\*,

n is 1 or 2,

when n is 1,

$R_1$  is hydrogen, alkyl of 1 to 18 carbon atoms, alkenyl of 2-18 carbon atoms, propargyl, glycidyl, alkyl of 2 to 50 carbon atoms interrupted by one to twenty oxygen atoms, said alkyl substituted by one to ten hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or

$R_1$  is alkyl of 1 to 4 carbon atoms substituted by a carboxy group or by -COOZ where Z is hydrogen, alkyl of 1 to 4 carbon atoms or phenyl, or where Z is said alkyl substituted by  $-(COO^-)_n M^{n+}$  where n is 1-3 and M is a metal ion from the 1st, 2nd or 3rd group of the periodic table or is Zn, Cu, Ni or Co, or M is a group  $N^{n+}(R_2)_4$  where  $R_2$  is alkyl of 1 to 8 carbon atoms or benzyl,

when n is 2,

$R_1$  is alkylene of 1 to 12 carbon atoms, alkenylene of 4 to 12 carbon atoms, xylylene or alkylene of 1 to 50 carbon atoms interrupted by one to twenty oxygen atoms, substituted by one to ten hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups,

in formula B and B\*,

m is 1 to 4,

when m is 1,

$R_2$  is alkyl of 1 to 18 carbon atoms, alkyl of 3 to 18 carbon atoms interrupted by  $-\text{COO}-$ , alkyl of 3 to 18 carbon atoms substituted by  $\text{COOH}$  or  $\text{COO}-$ , or  $R_2$  is  $-\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$  where n is 1 to 12, or

$R_2$  is cycloalkyl of 5 to 12 carbon atoms, aryl of 6 to 12 carbon atoms, or said aryl substituted by one to four alkyl groups of 1 to 4 carbon atoms, or

$R_2$  is  $-\text{NHR}_3$  where  $R_3$  is alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aryl of 6 to 12 carbon atoms, or said aryl substituted by one to four alkyl of 1 to 4 carbon atoms, or

$R_2$  is  $-\text{N}(\text{R}_3)_2$  where  $R_3$  is as defined above,

when m is 2,

$R_2$  is alkylene of 1 to 12 carbon atoms, alkenylene of 4 to 12 carbon atoms, xylylene, alkylene of 2 to 12 carbon atoms interrupted by  $-\text{COO}-$ , alkylene of 3 to 18 carbon atoms substituted by  $\text{COOH}$  or  $\text{COO}-$ , or  $R_2$  is  $-\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OCH}_2-$  where n is 1 to 12, or

$R_2$  is cycloalkylene of 5 to 12 carbon atoms, aralkylene of 7 to 15 carbon atoms or arylene of 6 to 12 carbon atoms, or

$R_2$  is  $-\text{NHR}_4\text{NH}-$  where  $R_4$  is alkylene of 2 to 18 carbon atoms, cycloalkylene of 5 to 12 carbon atoms, aralkylene of 8 to 15 carbon atoms or arylene of 6 to 12 carbon atoms, or

$R_2$  is  $-\text{N}(\text{R}_3)\text{R}_4\text{N}(\text{R}_3)-$  where  $R_3$  and  $R_4$  are as defined above, or

$R_2$  is -CO- or -NH-CO-NH-,

when  $m$  is 3,

$R_2$  is alkanetriyl of 3 to 8 carbon atoms or benzenetriyl, or

when  $m$  is 4,

$R_2$  is alkanetetrayl of 5 to 8 carbon atoms or benzenetetrayl,

in formula C and C\*,

$R_{10}$  is hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, alkanoyl of 2 to 18 carbon atoms, alkenoyl of 3 to 5 carbon atoms or benzoyl,

$x$  is 1 or 2,

when  $x$  is 1,

$R_{11}$  is hydrogen, alkyl of 1 to 18 carbon atoms, alkenyl of 2 to 18 carbon atoms, propargyl, glycidyl, alkyl of 2 to 50 carbon atoms interrupted by one to twenty oxygen atoms, said alkyl substituted by one to ten hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or

$R_{11}$  is alkyl of 1 to 4 carbon atoms substituted by a carboxy group or by -COOZ where Z is hydrogen, alkyl of 1 to 4 carbon atoms or phenyl, or where Z is said alkyl substituted by  $-(COO^-)_n M^{n+}$  where  $n$  is 1-3 and M is a metal ion from the 1st, 2nd or 3rd group of the periodic table or is Zn, Cu, Ni or Co, or M is a group  $N^{n+}(R_2)_4$  where  $R_2$  is hydrogen, alkyl of 1 to 8 carbon atoms or benzyl, or

when x is 2,

$R_{11}$  is alkylene of 1 to 12 carbon atoms, alkenylene of 4 to 12 carbon atoms, xylylene or alkylene of 1 to 50 carbon atoms interrupted by one to twenty oxygen atoms, substituted by one to ten hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups,

in formula D and D\*,

$R_{10}$  is as defined above,

y is 1 to 4, and

$R_{12}$  is defined as  $R_2$  above,

in formula E and E\*,

k is 1 or 2,

when k is 1,

$R_{20}$  and  $R_{21}$  are independently alkyl of 1 to 12 carbon atoms, alkenyl of 2 to 12 carbon atoms or aralkyl of 7 to 15 carbon atoms, or  $R_{20}$  is also hydrogen, or

$R_{20}$  and  $R_{21}$  together are alkylene of 2 to 8 carbon atoms or said alkylene substituted by hydroxyl, or are acyloxy-alkylene of 4 to 22 carbon atoms, or

when k is 2,

$R_{20}$  and  $R_{21}$  are together  $(-CH_2)_2C(CH_2)_2$ ,

in formula F and F\*,



R<sub>30</sub> is hydrogen, alkyl of 1 to 18 carbon atoms, benzyl, glycidyl, or alkoxyalkyl of 2 to 6 carbon atoms,

g is 1 or 2,

when g is 1, R<sub>31</sub> is defined as R<sub>1</sub> above when n is 1,

when g is 2, R<sub>31</sub> is defined as R<sub>1</sub> above when n is 2,

in formula G and G\*,

Q<sub>1</sub> is -NR<sub>41</sub>- or -O-,

E<sub>1</sub> is alkylene of 1 to 3 carbon atoms, or E<sub>1</sub> is -CH<sub>2</sub>-CH(R<sub>42</sub>)-O- where R<sub>42</sub> is hydrogen, methyl or phenyl, or E<sub>1</sub> is -(CH<sub>2</sub>)<sub>3</sub>-NH- or E<sub>1</sub> is a direct bond,

R<sub>40</sub> is hydrogen or alkyl of 1 to 18 carbon atoms,

R<sub>41</sub> is hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms, or R<sub>41</sub> is -CH<sub>2</sub>-CH(R<sub>42</sub>)-OH where R<sub>42</sub> is as defined above,

in formula H and H\*,

p is 1 or 2,

T<sub>4</sub> is as defined for R<sub>11</sub> when x is 1 or 2,

M and Y are independently methylene or carbonyl, preferably M is methylene and Y is carbonyl,

in formula I and I\*,

this formula denotes a recurring structural unit of a polymer where  $T_1$  is ethylene or 1,2-propylene or is the repeating structural unit derived from an alpha-olefin copolymer with an alkyl acrylate or methacrylate, and where

q is 2 to 100,

$Q_1$  is  $-N(R_{41})-$  or  $-O-$  where  $R_{41}$  is as defined above,

in formula J and J\*,

r is 1 or 2,

$T_7$  is as defined for  $R_1$  when n is 1 or 2 in formula A,

in formula L and L\*,

u is 1 or 2,

$T_{13}$  is as defined for  $R_1$  when n is 1 or 2 in formula A, with the proviso that  $T_{13}$  is not hydrogen when u is 1,

in formula M and M\*,

$E_1$  and  $E_2$ , being different, each are  $-CO-$  or  $-N(E_5)-$  where  $E_5$  is hydrogen, alkyl of 1 to 12 carbon atoms or alkoxy carbonylalkyl of 4 to 22 carbon atoms,

$E_3$  is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl, said phenyl or said naphthyl substituted by chlorine or by alkyl of 1 to 4 carbon atoms, or phenylalkyl of 7 to 12 carbon atoms, or said phenylalkyl substituted by alkyl of 1 to 4 carbon atoms,

$E_4$  is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl or phenylalkyl of 7 to 12 carbon atoms, or

$E_3$  and  $E_4$  together are polymethylene of 4 to 17 carbon atoms, or said polymethylene substituted by one to four alkyl of 1 to 4 carbon atoms, preferably methyl,

in formula N and N\*,

$R_1$  is as defined for  $R_1$  in formula A when n is 1,

$G_3$  is a direct bond, alkylene of 1 to 12 carbon atoms, phenylene or  $-NH-G_1-NH-$  where  $G_1$  is alkylene of 1 to 12 carbon atoms,

in formula O and O\*,

$R_{10}$  is as defined for  $R_{10}$  in formula C,

in formula P and P\*,

$E_6$  is an aliphatic or aromatic tetravalent radical, preferably neopentantetrayl or benzenetetrayl,

in formula T and T\*,

$R_{51}$  is hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, or aryl of 6 to 10 carbon atoms,

$R_{52}$  is hydrogen or alkyl of 1 to 18 carbon atoms, or

$R_{51}$  and  $R_{52}$  together of alkylene of 4 to 8 carbon atoms,

f is 1 or 2,

when f is 1,

$R_{50}$  is as defined for  $R_{11}$  in formula C when x is 1, or  $R_{50}$  is  $-(CH_2)_zCOOR_{54}$  where z is 1 to 4 and  $R_{54}$  is hydrogen or alkyl of 1 to 18 carbon atoms, or  $R_{54}$  is a metal ion from the 1st, 2nd or 3rd group of the periodic table or a group  $-N(R_{55})_4$  where  $R_{55}$  is hydrogen, alkyl of 1 to 12 carbon atoms or benzyl,

when f is 2,  $R_{50}$  is as defined for  $R_{11}$  in formula C when x is 2,

in formula U and  $U^*$ ,

$R_{53}$ ,  $R_{54}$ ,  $R_{55}$  and  $R_{56}$  are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene.

in formula V and  $V^*$ ,

$R_{57}$ ,  $R_{58}$ ,  $R_{59}$  and  $R_{60}$  are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene.

in formula W and  $W^*$ ,

$R_{61}$ ,  $R_{62}$ ,  $R_{63}$  and  $R_{64}$  are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene,

$R_{65}$  is alkyl of 1 to 5 carbon atoms,

M is hydrogen or oxygen,

wherein in formulas X to CC and  $X^*$  to  $CC^*$

n is 2 to 3,

G<sub>1</sub> is hydrogen, methyl, ethyl, butyl or benzyl,

m is 1 to 4,

x is 1 to 4,

when x is 1, R<sub>1</sub> and R<sub>2</sub> are independently alkyl of 1 to 18 carbon atoms, said alkyl interrupted by one to five oxygen atoms, said alkyl substituted by 1 to 5 hydroxyl groups or said alkyl both interrupted by said oxygen atoms and substituted by said hydroxyl groups; cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one to three alkyl of 1 to 8 carbon atoms, or R<sub>1</sub> is also hydrogen,

or R<sub>1</sub> and R<sub>2</sub> are together tetramethyl, pentamethylene, hexamethylene or 3-oxapentamethylene,

when x is 2,

R<sub>1</sub> is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or said alkyl both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

R<sub>2</sub> is alkylene of 2 to 18 carbon atoms, said alkylene interrupted by one to five oxygen atoms, said alkylene substituted by 1 to 5 hydroxyl groups or said alkylene both interrupted by said oxygen atoms and substituted by said hydroxyl groups; o-, m- or p-phenylene or said phenylene substituted by one or two alkyl of 1 to 4 carbon atoms, or

R<sub>2</sub> is  $-(CH_2)_kO[(CH_2)_kO]_h(CH_2)_k-$  where k is 2 to 4 and h is 1 to 40, or

R<sub>1</sub> and R<sub>2</sub> together with the two N atoms to which they are attached are piperazin-1,4-diyl,

when x is 3,

$R_1$  is hydrogen,

$R_2$  is alkylene of 4 to 8 carbon atoms interrupted by one nitrogen atom,

when  $x$  is 4,

$R_1$  is hydrogen,

$R_2$  is alkylene of 6 to 12 carbon atoms interrupted by two nitrogen atoms,

$R_3$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

$p$  is 2 or 3, and

$Q$  is an alkali metal salt, ammonium or  $N^+(G_1)_4$ ,

and in formula DD and DD\*

$m$  is 2 or 3,

when  $m$  is 2,  $G$  is  $-(CH_2CHR-O)_rCH_2CHR-$ , where  $r$  is 0 to 3, and  $R$  is hydrogen or methyl, and

when  $m$  is 3,  $G$  is glyceryl,

in formula EE and EE\*

$G_2$  is  $-CN$ ,  $-CONH_2$  or  $-COOG_3$  where  $G_3$  is hydrogen, alkyl of 1 to 18 carbon atoms or phenyl,

X is an inorganic or organic anion,

where the total charge of cations h is equal to the total charge of anions j, and with the proviso that bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate or the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid are excluded; and

wherein in formulas III to IIIc

A<sub>11</sub> is OR<sub>101</sub> or NR<sub>111</sub>R<sub>112</sub>

R<sub>101</sub> is alkenyl of 2 to 4 carbon atoms, propargyl, glycidyl, alkyl of 2 to 6 carbon atoms interrupted by one or two oxygen atoms, substituted by one to three hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or R<sub>101</sub> is alkyl of 1 to 4 carbon atoms substituted by carboxy or by the alkali metal, ammonium or C<sub>1</sub>-C<sub>4</sub>alkylammonium salts thereof; or R<sub>101</sub> is alkyl substituted by -COOE<sub>10</sub> where E<sub>10</sub> is methyl or ethyl,

R<sub>102</sub> is alkyl of 3 to 5 carbon atoms interrupted by -COO- or by -CO, or R<sub>102</sub> is -CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>c</sub>OCH<sub>3</sub> where c is 1 to 4; or

R<sub>102</sub> is -NHR<sub>103</sub> where R<sub>103</sub> is alkyl of 1 to 4 carbon atoms, a is 2 to 4,

when a is 2, T<sub>11</sub> is -(CH<sub>2</sub>CHR<sub>100</sub>-O)<sub>d</sub>CH<sub>2</sub>CHR<sub>100</sub>-, where d is 0 or 1, and R<sub>100</sub> is hydrogen or methyl,

when a is 3, T<sub>11</sub> is glyceryl,

when a is 4, T<sub>11</sub> is neopentetetrayl,

b is 2 or 3,

when b is 2, G<sub>11</sub> is -(CH<sub>2</sub>CHR<sub>100</sub>-O)<sub>e</sub>CH<sub>2</sub>CHR<sub>100</sub>-, where e is 0 to 3, and R<sub>100</sub> is hydrogen or methyl, and

when b is 3, G<sub>11</sub> is glyceryl;

R<sub>111</sub> is hydrogen, alkyl of 1 to 4 carbon atoms, or said alkyl substituted by one or two hydroxyl, interrupted by one or two oxygen atoms, or both substituted by one hydroxyl and interrupted by one or two oxygen atoms,

R<sub>112</sub> is -CO-R<sub>113</sub> where R<sub>113</sub> has the same meaning as R<sub>111</sub>, or R<sub>113</sub> is -NHR<sub>114</sub> wherein R<sub>114</sub> is alkyl of 1 to 4 carbon atoms, said alkyl substituted by one or two hydroxyl, substituted by alkoxy of 1 to 2 carbon atoms, or said alkyl both substituted by one hydroxyl and by one alkoxy of 1 to 2 carbon atoms, or

R<sub>111</sub> and R<sub>112</sub> together are -CO-CH<sub>2</sub>CH<sub>2</sub>-CO-, -CO-CH=CH-CO- or -(CH<sub>2</sub>)<sub>6</sub>-CO-; and with the proviso that, when R<sub>113</sub> is alkyl of 1 to 4 carbon atoms, R<sub>111</sub> is not hydrogen.

7. A composition according to claim 6 wherein the compound of component (b) is selected from the compounds of formulas A, A\*, B, B\*, C, C\*, D, D\*, Q, Q\*, R, R\*, S or S\*, X, X\*, Y, Y\*, Z and Z\*

where E is oxyl or hydroxyl, and R is hydrogen,

in formula A and A\*

n is 1 or 2,

when n is 1,

R<sub>1</sub> is hydrogen, alkyl of 1 to 6 carbon atoms, alkenyl of 2-6 carbon atoms, propargyl, glycidyl, alkyl of 2 to 20 carbon atoms interrupted by one to ten oxygen atoms, said alkyl substituted by one to five hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or

R<sub>1</sub> is alkyl of 1 to 4 carbon atoms substituted by a carboxy group or by -COOZ where Z is hydrogen or alkyl of 1 to 4 carbon atoms,

when n is 2,

R<sub>1</sub> is alkylene of 1 to 8 carbon atoms, alkenylene of 4 to 8 carbon atoms, alkylene of 1 to 20 carbon atoms interrupted by one to ten oxygen atoms, substituted by one to five hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups,

in formula B and B\*

m is 1 or 2



when m is 1,

$R_2$  is alkyl of 1 to 4 carbon atoms or  $R_2$  is  $\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$  where n is 1 to 12, or

$R_2$  is phenyl, or said phenyl substituted by one to three methyl groups,

$R_2$  is  $-\text{NHR}_3$  where  $R_3$  is alkyl of 1 to 4 carbon atoms or phenyl, or said phenyl substituted by one or two methyl groups,

when m is 2,

R is alkylene of 1 to 8 carbon atoms, alkenylene of 4 to 8 carbon atoms, or  $R_2$  is  $-\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OCH}_2-$  where n is 1 to 12,

$R_2$  is  $\text{NHR}_4\text{NH}$  where  $R_4$  is of 2 to 6 carbon atoms, aralkylene of 8 to 15 carbon atoms or arylene of 6 to 12 carbon atoms,

$R_2$  is  $-\text{CO}-$  or  $-\text{NHCONH}-$ ,

in formula C and C\*,

$R_{10}$  is hydrogen or, alkanoyl of 1 to 3 carbon atoms,

x is 1 or 2,

when x is 1,

$R_{11}$  is hydrogen, alkyl of 1 to 6 carbon atoms or glycidyl,

$R_{11}$  is alkyl of 1 to 4 carbon atoms substituted by a carboxy group or by  $\text{COOZ}$  where Z is hydrogen or alkyl of 1 to 4 carbon atoms,

when  $x$  is 2,

$R_{11}$  is alkylene of 1 to 6 carbon atoms,

in formula D and  $D^*$ ,

$R_{10}$  is hydrogen,

$y$  is 1 or 2,

$R_{12}$  is defined as  $R_2$  above,

in formula Y,  $Y^*$ , Z and  $Z^*$ ,

$x$  is 1 or 2,

when  $x$  is 1,

$R_1$  and  $R_2$  are independently alkyl of 1 to 4 carbon atoms,

or  $R_1$  and  $R_2$  are together tetramethylene, or pentamethylene,

$R_2$  is hydrogen or alkyl of 1 to 4 carbon atoms, said alkyl group substituted by a hydroxyl group,

when  $x$  is 2,

$R_1$  is hydrogen, alkyl of 1 to 4 carbon atoms, said alkyl substituted by a hydroxyl group,

$R_2$  is alkylene of 2 to 6 carbon atoms,

R<sub>10</sub> is hydrogen or alkanoyl of 1 or 2 carbon atoms,

x is 1 or 2,

when x is 1,

R<sub>11</sub> is hydrogen, alkyl of 1 to 4 carbon atoms or glycidyl,

R<sub>11</sub> is alkyl of 1 to 4 carbon atoms substituted by COOZ where Z is hydrogen or alkyl of 1 to 4 carbon atoms,

when x is 2,

R<sub>11</sub> is alkylene of 1 to 6 carbon atoms,

in formula D and D\*,

R<sub>10</sub> is hydrogen,

y is 1 or 2,

R<sub>12</sub> is defined as R<sub>2</sub> above.

9. A composition according to claim 6 wherein the compound of component (b) is

- (a) bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
- (b) bis(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
- (c) 1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium citrate;
- (d) 1-oxyl-2,2,6,6-tetramethyl-4-acetamidopiperidine;
- (e) 1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidine;
- (f) 1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium bisulfate;
- (g) 1-oxyl-2,2,6,6-tetramethyl-4-oxo-piperidine;

$R_3$  is as defined above.

8. A composition according to claim 7 wherein the compound of component (b) is selected from the compounds of formulas A, A\*, B, B\*, C, C\*, D, D\*, Q, Q\*, R and R\*

where E is oxyl or hydroxyl,

R is hydrogen,

in formula A and A\*,

h is 1,

$R_1$  is hydrogen, alkyl of 1 to 4 carbon atoms, glycidyl, alkyl of 2 to 4 carbon atoms interrupted by one or two oxygen atoms, said alkyl substituted by one or two hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or

$R_1$  is alkyl of 1 to 4 carbon atoms substituted by -COOZ where Z is hydrogen or alkyl of 1 to 4 carbon atoms,

in formula B and B\*,

m is 1 or 2,

$R_2$  is alkyl of 1 to 4 carbon atoms or  $R_2$  is  $\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$  where n is 1 to 4,

when m is 2,

R is alkylene of 1 to 8 carbon atoms,

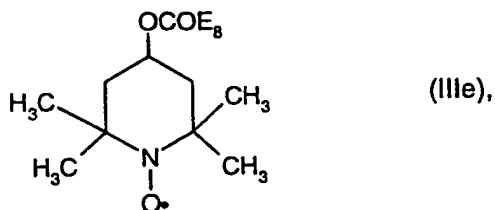
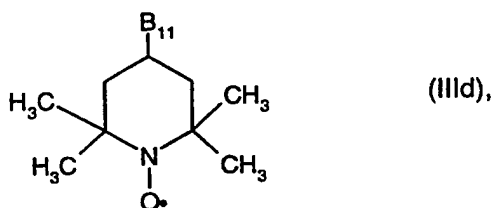
in formula C and C\*,

- (hh) tri(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) nitrilotriacetate;  
 (ii) tri(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) nitrilotriacetate;  
 (jj) tri(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium) nitrilotriacetate;  
 (kk) penta(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium)  
 diethylenetriaminepentamethylenephosphonate;  
 (ll) penta(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium)  
 diethylenetriaminepentamethylenephosphonate;  
 (mm) penta(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium)  
 diethylenetriaminepentamethylenephosphonate.

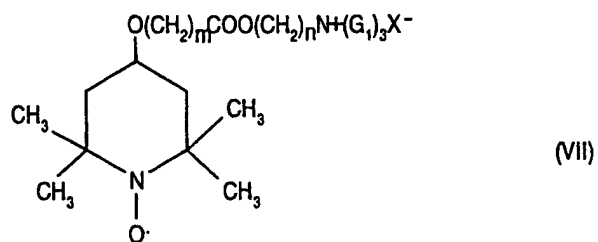
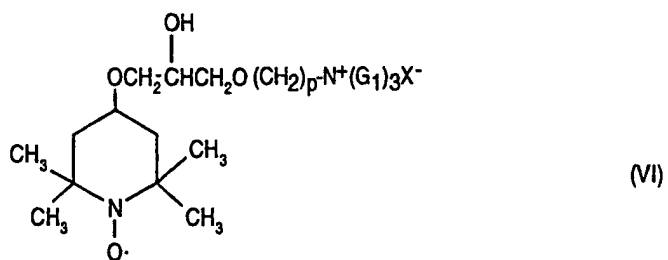
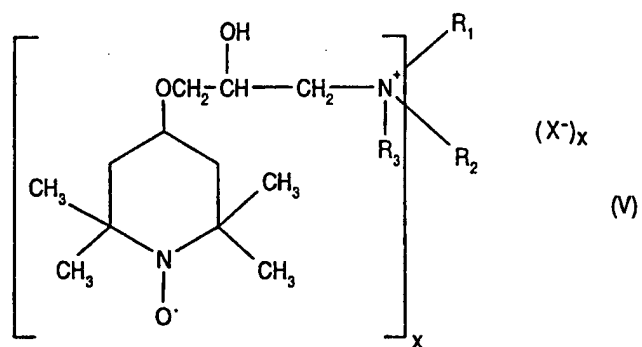
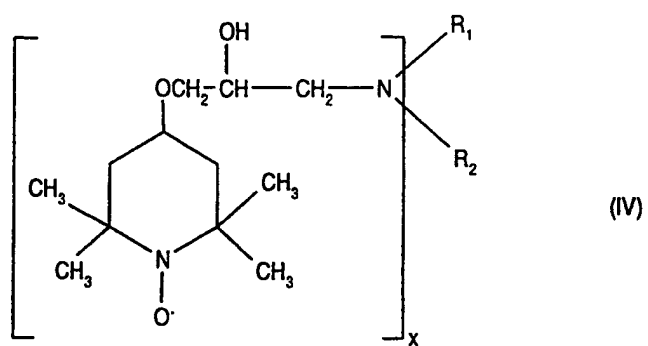
10. A composition according to claim 1 wherein the effective amount of the hindered amine compound of component (b) is 0.001 to 5% by weight based on the pulp or paper.

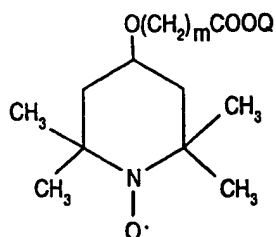
11. A composition according to claim 1 which additionally includes an effective stabilizing amount of at least one coadditive selected from the group consisting of the UV absorbers, the polymeric inhibitors, the fluorescent whitening agents and metal chelating agents and mixtures thereof.

12. A compound of formula IIIId, IIIe, IV, V, VI, VII or VIII



- (h) 1-hydroxy -2,2,6,6-tetramethyl-4-oxo-piperidine;
- (i) 1-hydroxy -2,2,6,6-tetramethyl-4-oxo-piperidinium acetate;
- (j) 1-oxyl-2,2,6,6-tetramethyl-4-methoxy-piperidine;
- (k) 1-hydroxy-2,2,6,6-tetramethyl-4-methoxy-piperidine;
- (l) 1-hydroxyl-2,2,6,6-tetramethyl-4-methoxy-piperidinium acetate;
- (m) 1-oxyl-2,2,6,6-tetramethyl-4-acetoxypiperidine;
- (n) 1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidine;
- (o) 1-oxyl-2,2,6,6-tetramethyl-4-propoxy-piperidine;
- (p) 1-hydroxy-2,2,6,6-tetramethyl-4-propoxy-piperidinium acetate;
- (q) 1-hydroxy-2,2,6,6-tetramethyl-4-propoxy-piperidine;
- (r) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxypiperidine);
- (s) 1-hydroxy-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxypiperidinium acetate);
- (t) 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine;
- (u) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidine;
- (v) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium chloride;
- (w) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium acetate;
- (x) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium bisulfate;
- (y) 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium citrate;
- (z) bis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) citrate;
- (aa) tris(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) citrate.
- (bb) tetra(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) ethylenediaminetetraacetate;
- (cc) tetra(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) ethylenediaminetetraacetate;
- (dd) tetra(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium) ethylenediaminetetraacetate;
- (ee) penta(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium) diethylenetriaminepentaacetate;
- (ff) penta(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium) diethylenetriaminepentaacetate;
- (gg) penta(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium) diethylenetriaminepentaacetate;





(VIII)

wherein in the formulas III d and III e

$B_{11}$  is  $OE_9$  or  $NE_{11}E_{12}$

$E_9$  is alkyl of 2 to 6 carbon atoms interrupted by one or two oxygen atoms, substituted by two to three hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or  $E_9$  is alkyl of 1 to 4 carbon atoms substituted by carboxy or by the alkali metal, ammonium or lower alkylammonium salts thereof; or  $E_9$  is alkyl substituted by  $-COOE_{10}$  where  $E_{10}$  is methyl or ethyl, and

$E_8$  is alkyl of 3 to 5 carbon atoms interrupted by  $-COO-$  or by  $-CO-$ , or  $E_8$  is  $-CH_2(OCH_2CH_2)_aOCH_3$  where  $a$  is 1 to 4; or

$E_8$  is  $-NHE_7$  where  $E_7$  is alkyl of 1 to 4 carbon atoms;

$E_{11}$  is hydrogen or alkyl of 1 to 4 carbon atoms, and

$E_{12}$  is  $-CO-E_{13}$  where  $E_{13}$  is alkyl of 1 to 4 carbon atoms which alkyl is interrupted by one or two oxygen atoms, or  $E_{13}$  is  $-NHE_{14}$  where  $E_{14}$  is alkyl of 1 to 4 carbon atoms; with the proviso that  $E_9$  is not 2,3-dihydroxypropyl,

and wherein in the formulas IV, V, VI, VII and VIII

$n$  is 2 to 3,

$G_1$  is hydrogen, methyl, ethyl, butyl or benzyl,

$X$  is inorganic or organic anion,

$m$  is 1 to 4,

$x$  is 1 to 4,



when x is 1,  $R_1$  and  $R_2$  are independently alkyl of 1 to 18 carbon atoms, said alkyl interrupted by one to five oxygen atoms, said alkyl substituted by 1 to 5 hydroxyl groups or said alkyl both interrupted by said oxygen atoms and substituted by said hydroxyl groups; cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one to three alkyl of 1 to 8 carbon atoms, or  $R_1$  is also hydrogen,

or  $R_1$  and  $R_2$  are together tetramethyl, pentamethylene, hexamethylene or 3-oxapentamethylene,

when x is 2,

$R_1$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or said alkyl both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

$R_2$  is alkylene of 2 to 18 carbon atoms, said alkylene interrupted by one to five oxygen atoms, said alkylene substituted by 1 to 5 hydroxyl groups or said alkylene both interrupted by said oxygen atoms and substituted by said hydroxyl groups; o-, m- or p-phenylene or said phenylene substituted by one or two alkyl of 1 to 4 carbon atoms, or

$R_2$  is  $-(CH_2)_kO[(CH_2)_kO]_h(CH_2)_k-$  where k is 2 to 4 and h is 1 to 40, or

$R_1$  and  $R_2$  together with the two N atoms to which they are attached are piperazin-1,4-diyl,

when x is 3,

$R_1$  is hydrogen,

$R_2$  is alkylene of 4 to 8 carbon atoms interrupted by one nitrogen atom,

when x is 4,

$R_1$  is hydrogen,

$R_2$  is alkylene of 6 to 12 carbon atoms interrupted by two nitrogen atoms,

$R_3$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

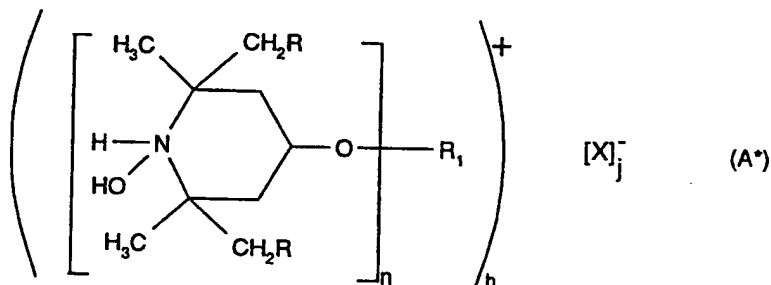
$p$  is 2 or 3, and

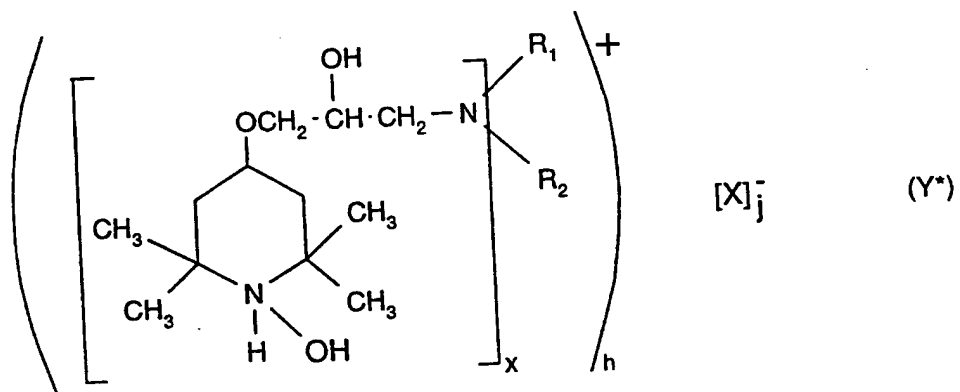
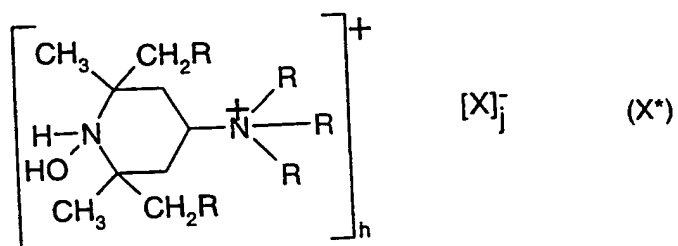
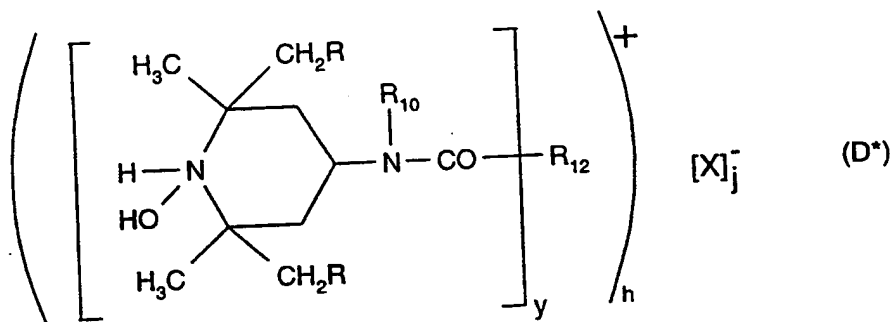
$Q$  is an alkali metal salt, ammonium or  $N^+(G_1)_4$ .

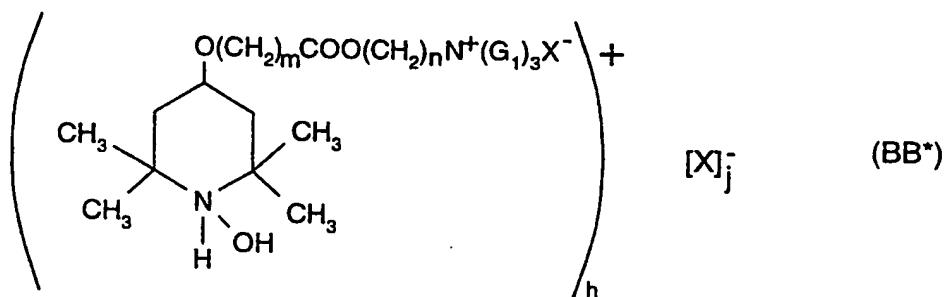
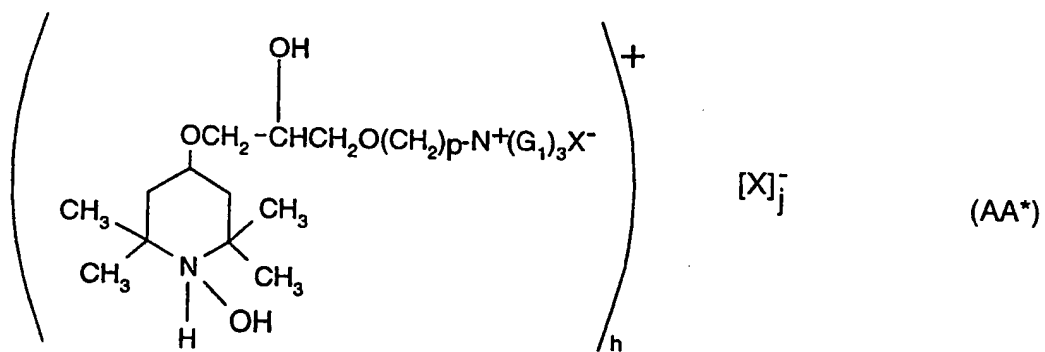
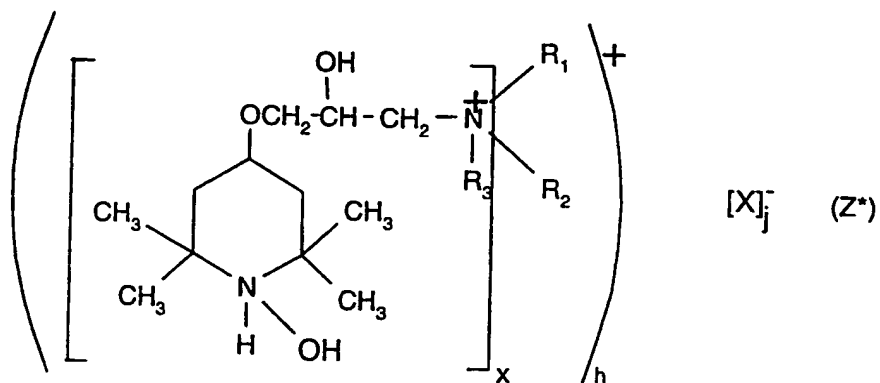
13. A compound according to claim 12 where in the compounds of formulas IV to VIII

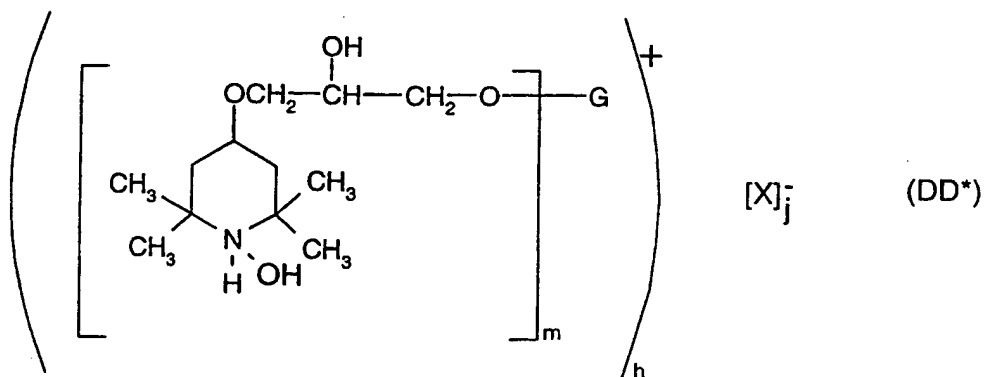
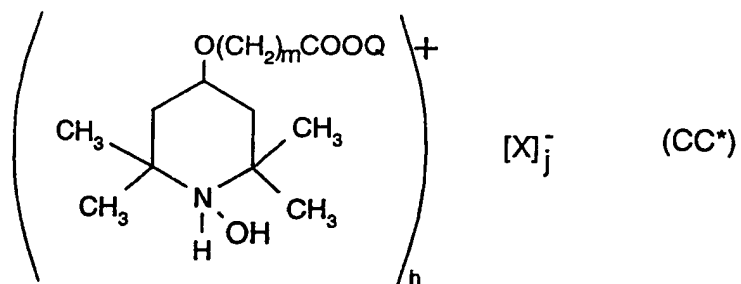
$n$  is 2;  $G_1$  is hydrogen or methyl;  $X$  is chloro or bromo;  $x$  is 1 or 2,  $R_1$  and  $R_2$  are independently alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or said alkyl both interrupted by one or two oxygen atoms and substituted by a hydroxyl group, or  $R_1$  is hydrogen; or  $R_1$  and  $R_2$  together are 3-oxapentamethylene;  $R_3$  is hydrogen or alkyl of 1 to 2 carbon atoms, or said alkyl substituted by a hydroxyl group,  $p$  is 2,  $m$  is 1, and  $Q$  is  $Na^+$ ,  $NH_4^+$  or  $N(CH_3)_4^+$ .

14. A hydroxylamine salt of formula  $A^*$ ,  $D^*$ ,  $X^*$ ,  $Y^*$ ,  $Z^*$ ,  $AA^*$ ,  $BB^*$ ,  $CC^*$  or  $DD^*$









R is hydrogen,

in formula A\*  
wherein

n is 1,

R<sub>1</sub> is hydrogen or alkyl of 1 to 4 carbon atoms, preferably hydrogen,

in formula D\*

y is 1,

R<sub>10</sub> is hydrogen or methyl, preferably hydrogen,

$R_{12}$  is alkyl of 1 to 4 carbon atoms, preferably methyl,

X is phosphate, phosphonate, carbonate, bicarbonate, nitrate, chloride, bromide, bisulfite, sulfite, bisulfate, sulfate, borate, formate, acetate, benzoate, citrate, oxalate, tartrate, acrylate, polyacrylate, fumarate, maleate, itaconate, glycolate, malate, mandelate, tiglate, gluconate, ascorbate, polymethacrylate, a carboxylate of nitrilotriacetic acid, hydroxyethylethylenediaminetriacetic acid, ethylenediaminetetraacetic acid or of diethylenetriaminepentaacetic acid, a diethylenetriaminepentamethylenephosphonate, an alkylsulfonate or an arylsulfonate,

where the total charge of cations  $h$  is equal to the total charge of anions  $j$ ,

wherein in formulas  $X^*$  to  $DD^*$

$n$  is 2 to 3,

$G_1$  is hydrogen, methyl, ethyl, butyl or benzyl,

$m$  is 1 to 4,

$x$  is 1 to 4,

when  $x$  is 1,  $R_1$  and  $R_2$  are independently alkyl of 1 to 18 carbon atoms, said alkyl interrupted by one to five oxygen atoms, said alkyl substituted by 1 to 5 hydroxyl groups or said alkyl both interrupted by said oxygen atoms and substituted by said hydroxyl groups; cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one to three alkyl of 1 to 8 carbon atoms, or  $R_1$  is also hydrogen,

or  $R_1$  and  $R_2$  are together tetramethylene, pentamethylene, hexamethylene or 3-oxapentamethylene,

when  $x$  is 2,

$R_1$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or said alkyl both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

$R_2$  is alkylene of 2 to 18 carbon atoms, said alkylene interrupted by one to five oxygen atoms, said alkylene substituted by 1 to 5 hydroxyl groups or said alkylene both interrupted by said oxygen atoms and substituted by said hydroxyl groups; o-, m- or p-phenylene or said phenylene substituted by one or two alkyl of 1 to 4 carbon atoms, or

$R_2$  is  $-(CH_2)_kO[(CH_2)_kO]_h(CH_2)_k-$  where  $k$  is 2 to 4 and  $h$  is 1 to 40, or

$R_1$  and  $R_2$  together with the two N atoms to which they are attached are piperazin-1,4-diyl,

when  $x$  is 3,

$R_1$  is hydrogen,

$R_2$  is alkylene of 4 to 8 carbon atoms interrupted by one nitrogen atom,

when  $x$  is 4,

$R_1$  is hydrogen,

$R_2$  is alkylene of 6 to 12 carbon atoms interrupted by two nitrogen atoms,

$R_3$  is hydrogen, alkyl of 1 to 8 carbon atoms, said alkyl interrupted by one or two oxygen atoms, said alkyl substituted by a hydroxyl group, or both interrupted by one or two oxygen atoms and substituted by a hydroxyl group,

$p$  is 2 or 3, and

Q is an alkali metal salt, ammonium or  $N^+(G_1)_4$ ,

in formula DD and DD\*

m is 2 or 3,

when m is 2, G is  $-(CH_2CHR-O)_rCH_2CHR-$ , where r is 0 to 3, and R is hydrogen or methyl, and

when m is 3, G is glyceryl,

with the proviso that in formula A\* when  $R_1$  is hydrogen, X is not chloride or bisulfate, and when in formula D\* when  $R_{10}$  is hydrogen and  $R_{12}$  is methyl, X is not chloride or bisulfate.

15. A process for preventing the loss of brightness and for enhancing resistance to yellowing of chemimechanical or thermomechanical pulp or paper which still contains lignin, which comprises

treating said pulp or paper with an effective stabilizing amount of a compound of formula I or II according to claim 1.

16. A process according to claim 15 where in the compound of formula I, E is oxyl or hydroxyl.

17. A process according to claim 15, wherein the compound of formula I or II is one of formula A to EE or A\* to EE\* or III to IIIc according to claim 6.

18. Use of a compound of formula I or II according to claim 1 for treating a chemimechanical or thermomechanical pulp or paper which still contains lignin against the loss of brightness and for enhancing resistance to yellowing.